NUMERICAL STUDY OF SEMICONDUCTOR MATERIAL GROWTH

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ABSTRACT

Nanostructured materials have greatly attracted people’s attention in the past ten years, because they become applicable not only in systems of academic interest, but also to systems of practical impact. In particular, semiconductor nanostructures have a large potential for applications in optoelectronics. On the other hand, computer modeling of nanostructured material has been developed very much, such as density-functional theory, molecular dynamics, and Monte Carlo method. Every method has its advantage in different applications.

In this work, three-dimensional quantum dots growth is studied by using kinetic Monte Carlo method. Thin film growth mechanism is well studied. Therefore, first of all thin film growth mechanism is reviewed. Then heteroepitaxy is discussed, including the strain energy effect on thin film growth and two-dimension to three-dimension transition. At last three-dimensional growth of quantum dots is illustrated. In this section, strain energy calculated from point eigen-strain instead of point /line force is extended from two-dimension to three-dimension. Furthermore, in three-dimensional growth an energy barrier, called Ehrlich-Schwoeble barrier, which hinders the descent of atoms to lower level is incorporated.

By using the 3D model, 3D InAs/GaAs QD island size and density evolution under different coverage and temperature is investigated. By comparing our simulation
results to experimental ones, we found that there is a size limit for growth coverage. Below the limit existing islands can adsorb more new coming adatoms; however, beyond the limit new islands will be formed to adopt new coming adatoms. We also observed that with increasing temperature, the islands size will increase while their density will decrease.

Various methods have been proposed recently for patterning the substrate so that overgrown QD islands with uniform lateral ordering and equal size distribution can be achieved. Such control may be used to tailor the optoelectronic properties during synthesis and subsequently exploit correlation effects among dots. In this work, we present computer simulations for QD island self-organization on pre-patterned substrates where the pattern control is achieved by adjusting the growth interruption time. Furthermore, correlation between the QD island pattern and substrate anisotropy (due to different crystalline orientations) can also be clearly observed.
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CHAPTER I
INTRODUCTION AND MOTIVATION

1.1 Introduction

Quantum dots (QDs) are a special class of materials known as semiconductors. The semiconductors are critical parts of many different kinds of electrical circuits and optical applications, since their electrical conductivity can be greatly altered via an external stimulus. QDs are unique class of semiconductor because they are so small; just

![Figure 1.1 Illustration of material structure and corresponding energy distribution. (a) 3-dimensional, (b) 2-dimensional, (c) 1-dimensional, (d) 0-dimensional.](image)
have 1~200 atoms in diameter and range from 2~10 nanometers. At these small sizes, materials behave differently, giving QDs unprecedented potential applications. One example is that their color depends on the size of the dot, thus it is possible to make structures with a wide variety of colors simply by varying the size of the dot.

A QD is something capable of confining exitons in three dimensions, and in which the electrons occupy discrete energy states just as they would in an atom. As a result, they have properties that are between those of bulk form and those of discrete molecules.

Talking about the application of QDs, light emitting diodes (LED) (Figure 1.2) is a very important one. QDs are valued for displays, because they emit light in very specific Gaussian distributions. This can result in a display more accurate colors than the human eye can perceive. QDs also require very little power since they are not color filtered.

![Figure 1.2 First white LED using QDs by Sandia National Laboratories.](image)

In the biological application, QDs also have been used as fluorescence tag. Unlike fluorescence dyes, QDs maintain their integrity which stands more cycles of excitation
and light emission before they start to fade. Since they are fluorescing in multicolor, it allows us to cater their optical properties just by changing their size or composition. However, QDs are soluble in water. In order to overcome this problem, the QDs are coated with polymer layer, which enables QDs mix with water. These types of structures can help to protect a chemically or electrically sensitive dot from an unfriendly environment.

There are two major fabrication methods for QDs. One is called top down method, like lithographic; the other is called bottom up, like self-organization.

In the first method, a lithographic process was used to create a two-dimensional (2D) structure that could be further etched down to isolate a QD. However, these QDs were only nanometer scale in one dimension that is the thickness of the semiconductor layer used to trap the electrons in the dot. The other two dimensions were typically confined by the resolution of the lithography, and could be as big as a micron.

The second fabrication method is called self-organization. In the last few years, nanostructures fabricated by using self-organization method have been successfully realized. These effects are also called self-ordering or self-assembly.¹ Combining thermodynamic and kinetic ordering mechanisms together can create unique three-dimensional (3D) patterns of islands within a matrix for many different material systems.

Self-organization is a process of attraction and repulsion in which the internal organization of a system, normally an open system, increases in complexity without being guided or managed by an outside source.

Researchers now began to grow “self-assembled” dots by depositing a semiconductor material with a larger lattice constant onto a semiconductor with a smaller
lattice constant, this is called strained epitaxial growth. Typical systems were germanium (Ge) on silicon (Si) and indium arsenide (InAs) on gallium arsenide (GaAs).

1.2 Motivation

For practicable applications in semiconductor devices, millions of the quantum structures, densely packed and uniform on the atomic scale are necessary to achieve the desired active volume. This requires more precise fabrication methods to provide better control of size and shape of large ensembles of nanostructures. Ultralow threshold currents with high temperature stability have been predicted for QD lasers and high mobility at room temperature in quantum-dot super lattices.2

A beautiful example of building nano-objects with atomic precision is the creation of quantum corrals3 and quantum mirages4 demonstrated by Eigler et al., using atom manipulation by scanning tunneling microscopy (STM). However, such an approach may not be suitable for mass production in device fabrication, because it is inherently a time-consuming serial process.

In self-assembly and self-organization approach, coherent 3D islands (free of dislocations) form spontaneously in strained thin films5—11. These 3D islands (clusters) form, in general, with crystalline perfection and nanometer dimensions, could be naturally used as QDs. This phenomenon has shown great promise for device fabrication because it offers an economical parallel process with the added advantage of being compatible with the existing Si processing technology.

Meanwhile, considerable recent research interest is attracted on study of morphological instability and ordering in strained thin films, since a strained thin film is
inherently unstable.\textsuperscript{12} Upon reaching the “equilibrium critical thickness”,\textsuperscript{13,14} a strained film will relax back to its equilibrium lattice constant, forming dislocations at the interface. Below the critical thickness, strain is partially relieved by surface roughening, which may manifest itself in various forms. Self-organization starts a new field for the research of strained thin films, the “strain engineering of nanostructures”\textsuperscript{12}.

However, fabrication of QDs with desirable uniformity remains, so far, a challenging problem. This is because our fundamental understanding of the physical and dynamical processes at the nanometer scale is still limited and it is very difficult to design and apply fabrication and characterization tools at the nanometer scale. Furthermore, leading experiment test on study of this fabrication method is expensive and the lack of control over positioning of individual dots. In order to overcome these limitations, the numerical simulation is proposed in this work to study the changes of QDs patterning with growth conditions in this work, since numerical modeling is of low cost and could be able to give guides to experiment.

1.3 Models of heteroepitaxial growth

There are three popular models for heteroepitaxial growth. They are density-functional theory (DFT), molecular dynamic (MD) and Monte Carlo simulations.

DFT (ref. 16) methods were used successfully in some cases for energy calculations in the situations such like found in heteroepitaxial growth, for example in ref.17. The advantage of this method is that very few assumptions about the electronic structure have to be made. However, with respect to the high computational load, it is impossible to use DFT for in–situ calculation of diffusion barriers. Only the calculation
of single events, e.g. the adsorption of an As$_2$ molecule on a GaAs surface at zero temperature and pressure, is within the scope of the method right now.$^{16}$

MD simulations are the most realistic method for the simulation of heteroepitaxial growth if at least an empirical potential for the interaction between particles of the system is given. However, restriction of MD simulation is the short physical times.

Monte Carlo simulations could be utilized for the simulation of heteroepitaxial growth by allowing for continuous particle distances in order to account for strain effects. Monte Carlo method of modeling QDs growth combining the microscopic events and macroscopic parameters gives a good resolution for the problem. The basis of a Monte Carlo simulation is single particle events, modeling single atom motion under particular environment. The time evolution of Monte Carlo method is using a Markov chain.

1.4 Structure of this work

This work adopted kinetic Monte Carlo method to study 3D strained QDs growth on cubic lattice based on solid model by incorporating elastic strain energy effect.

Monte Carlo method is widely used these days to study the homoepitaxial growth. It is a method based on statistical theory, and its basic idea will be introduced in next chapter. Important mechanisms concerning particle motion and QDs growth are discussed at the same time. Concept of energy barrier is also introduced.

The strain distribution in a growing sample is one of the main driving forces leading to the formation of nanostructures, and it also influences the particularities of their growth and arrangement. This can lead to very regular ensembles of nanostructures, with narrow size distribution, lined up in more or less perfect one-, two-, or even three-
dimensional lattices. A main effect here is that the strain field of a small buried island influences the nucleation of islands at the growth surface, even if the surface undulations due to the buried structure have already vanished. In the next chapter, the calculation and consideration of strain energy will be discussed in detail.

Due to the fact that the island nucleation process is statistical in nature, usually the size distribution of self-organized islands is fairly broad. However, island distribution is an important factor in applications, which largely influences the device function. By using this 3D cubic lattice model, density and size distribution of QDs influenced by experimental conditions is analyzed in Chapter 3.

In the fabrication industry, an important method to get ordered QDs pattern is called prepattern method, in which QDs further grow on top of patterned substrate to guarantee the lateral order of QDs. During this process, strain energy which serves as a nucleation site plays an important role when QDs grow. Relevant theory and simulation method regarding to prepattern growth are studied in Chapter 4.

Self-organization growth is a new way to obtain required QDs products. Many aspects in this domain, no matter theory or experiment, are not well developed, and many works are waiting to be done. In Chapter 5, future work concerning this study is discussed.
CHAPTER II
MONTE CARLO SIMULATION OF SELF-ORGANIZED QUANTUM DOT GROWTH

2.1 Growth mechanisms of self-organized QDs

Process of QDs growth is a complex procedure including atoms deposition, adsorption and desorption of atoms, atoms movement on the surface, nucleus formation, QDs growth, QDs moving on the surface. Actually growth of QDs from atoms deposited from the gas phase is a non-equilibrium phenomenon governed by a competition between kinetics and thermodynamics. Precise control of the growth and thus of the properties of deposited films becomes possible only after an understanding of this competition is achieved.

As it is well known that adatoms will behave different when encounter different situation. Further understanding of atomic nature of most important kinetic mechanisms helps to modify the numerical model and to give more accurate results comparing to reality. In this section, the most important atomic mechanisms of QD growth on cubic lattice are described. These mechanisms include adatoms diffusion on terraces, along steps, and around island corners; nucleation of the stable nucleus; atom attachment to and detachment from terraces and islands; interlayer mass transport; and misfit strain influence.
However, our model is set up on a cubic lattice, some important mechanisms effects in real structure model are missing. Moreover, atoms vibrations depending on temperature and misfit thermal strain by different temperature are not included. This leads to a simplified model and less work to be done, but will fail to show some phenomenon related to mechanisms appearing in real structures. However, from this simplified model, some important properties are able to be revealed. It is the foundation of further development of real structure model.

2.1.1 Terrace-step-kink model

Terrace-step-kink (TSK) model (Figure 2.1),\textsuperscript{18} developed by Burton, Cabrera and Frank in the early 1950s, describes the atomic-scale morphology of the surface of a crystal.

In this model, complicated surface environment has been simplified and distinguished into four representative situations. As shown in figure 2.1, they are flat surface, terrace, step, and kink. Adatoms can diffuse on top of the surfaces, terraces, and steps; can move along terrace, steps, and kinks. Moreover, adatoms can also hop across terraces and steps which are called interlayer mass transport.

However, the motion of the adatoms is a competition process between kinetics and thermodynamics as we mentioned in last section, but it is mostly determined by the free energy. Energy encountered by adatoms is determined by the interaction of atoms. Therefore the relative position of adatoms and other atoms in the system will influence the magnitude of free energy and will further influence the motion of adatoms.
Figure 2.1 Terrace-step-kink (TSK) model shows substrate surface, step, and 3D terrace by color blue from dark to light. Nanostructures formed by adatoms are shown in red color. They are single adatom, dimer, and island.

Besides structures mentioned above, there are also some important elements formed by adatoms such as dimmers, nucleus, and islands. These small structures will also affect the motion of new coming adatoms. Nucleus is relatively a stable structure comparing to a single adatom, and it can attract more atoms to form larger assemble. When more and more adatoms are attracted by the nucleus, island is formed and grown.

When come to heteroepitaxial growth, there is a very important factor called misfit strain which affects the final surface morphology and lead the system from thin film growth to 3D growth. Misfit strain and 3D growth will be discussed in section 2.1.4.

Moreover, besides basic phenomenon, final surface morphology will also be affected by many other important factors, such as the deposition and adsorption process. All these mechanisms will be discussed in the following sections.
2.1.2 Deposition technique

The act of applying atoms to a surface is known as deposition. Thin-film deposition is any technique for depositing a thin film of material onto a substrate or onto previously deposited layers. So far many methods have been explored for particles deposition used in semiconductor growth. Overall, it falls into two broad categories, depending on whether the process is primarily chemical or physical. During chemical deposition it occurs via chemical reactions of precursor at the sample surface, while for physical deposition mechanical or thermodynamic means is used to produce a thin film of solid.

Molecular beam epitaxy (MBE) is a widely used method in semiconductor deposition. It is a kind of physical deposition method. Take Ga and As deposition for example, the precursors are heated to vapor separately. Then the material beam is slowly deposited onto the surface. Under the ultra high vacuum, Ga and As may react with each other on the substrate surface. Evaporated atoms don’t interact with each other or vacuum chamber gases until they reach the wafer. Since no other chemically active substances are used in this form of epitaxy, deposition and diffusion are the most basic processes. Therefore the growth technique of MBE is very convenient for theoretical modeling of growth.19

In semiconductor industry, Chemical vapor deposition (CVD) is another widely used deposition method, which is a chemical process. In a typical CVD process, the substrate is exposed to one or more volatile precursors, which decompose and react on the substrate surface to produce the desired deposit. Frequently, volatile by-products are
also produced, which are removed by gas flow through the reaction chamber. The numerical model of the CVD process will be more complex than the MBE one. Besides the evolution of the atomic structure at the growth surface, reaction kinetics in the vapor and at the surface should also be considered in the numerical model. 20

2.1.3 Adatom diffusion during thin film growth

Adatom diffusion is the main kinetic process in film growth. During this process, nanostructures are formed and material surface are formed. In this section diffusion is distinguished into several categories. They are diffusion on the flat surface or terrace, formation of nucleus, diffusion along edges, kink, and detachment, diffusion across steps.

2.1.3.1 Diffusion on the flat surface or terrace

Atoms are deposited onto the surface at a random location with certain speed. When substrate is heated the adatoms gain a new thermodynamic energy which makes adatoms more active to jump to new position. It will diffuse on the surface until it finds a stable state to stay. The diffusion of an adatom on a flat surface, or terrace, is by far the most important kinetic process in film growth. Smooth, uniform films could not be formed without sufficient surface mobility.

The adatom may have multiple diffusion pathways on the surface before finding a stable state. In the initial stage, adatom will first relax to a local minimum, rather than directly to a stable adsorption site. 21 Adatoms prefer first hopping to metastable site with less kinetic energy than to stable site directly with more energy. If the potential-energy barrier for the adatom to reach a stable site is much higher than the barrier for it to reach
an metastable site, then the adatom will travel a path connecting the metastable sites before reaching a stable site.

2.1.3.2 Stable nucleus

When adatoms meet each other to form an island, interaction bonds between adatoms are formed, which reduce the free energy of the island and protect the island from decomposition. However, adatoms at the edges of the island have more unsaturated bonds comparing to atoms inside the island. Unsaturated bonds make the island unstable. Boundary atoms proportion of island will decide whether the island is stable or not.

Recent studies have often suggested that, at sufficiently low temperatures, for typical growth conditions, the adatom supersaturation on the surface is so high that the critical nucleus is just a single atom, and the stable nucleus is two atoms, a dimer.\textsuperscript{22}

These dimers then serve as the centers for growth of larger islands, as more adatoms diffuse to meet them. Precisely how atoms attach to stable dimmers to form those various islands is unknown.

2.1.3.3 Diffusion along edges, kink, and detachment

When adatom diffuses along the island edge (Figure 2.2 (a)), it has to pass through a succession of intermediate states where it is in contact with a smaller number of adatoms, which makes it difficult to diffuse along the edge. When encounter the island corner (Figure 2.2 (b)) where two edges meet (the kink site), it is more difficult to cross it. The reason for this is the adatom has to further lower its coordination when crossing a corner. For the case of detachment (Figure 2.2 (c)), the adatom has to lose all the
neighbors connection. Therefore the energy need to detach from the island is larger than to cross the corner. The energy need to diffuse along the island is the smallest of the three.

![Figure 2.2 Schematic illustration of diffusions in the horizontal (x,y)-plane. (a) edge diffusion, (b) corner diffusion, (c) off diffusion.](image)

2.1.3.4 Diffusion crossing steps

Adatoms can have two paths to get down the step, hopping and exchange. During hopping diffusion (Figure 2.3 (b)) the adatoms at the edge on top of the island hop over edge of the island down to the lower layer. However, for exchange diffusion (Figure 2.3 (c)), the adatom replaces a surface atom and this surface atom a diffusion along the surface.

The atom on a terrace has a certain number of nearest neighbors which provide stability for that atom through atomic bond (Figure 2.3 (a)). When it reaches the edge of a terrace, it has fewer neighbors as shown in Figure 2.3 (a). In this way the balance of the bonds felt by adatom is broken up, which result in a barrier for diffusion over the edge. The energy barrier acts like a reflective wall at the edge of a terrace, which became
known as the Ehrlich–Schwoebel (ES) barrier, hindering the descent of atoms to lower levels.\textsuperscript{24} This increases the chance of nucleation and growth of a new film layer. Research found that there exist a critical thickness, beyond which a 2D to 3D growth will occur.\textsuperscript{30,31}

ES barrier has been widely studied for different material, such as copper\textsuperscript{25} and silver.\textsuperscript{26} Many numerical models dealing with 3D QD growth set up based on this ES barrier have been developed and used for studying QDs growth. Such work can be found in ref.\textsuperscript{27~29}.

2.1.3.5 Strain influence

If adsorbate material is deposited onto a substrate with a different lattice constant comparing to that of adsorbate material, strained-layer heteroepitaxy occurs.
Misfit describes difference of lattice constant of two materials, and is defined as
\[ \varepsilon = \frac{a_a - a_s}{a_s} \]  
whereas \( a_a \) is lattice constant of adsorbate material, \( a_s \) lattice constant of substrate material. For example, the lattice constant of InAs is 6.0584Å at 300K, and the lattice constant of GaAs is 5.6533Å at 300K. The melting point is much higher than the temperature. If we deposit InAs onto GaAs, heteroepitaxy will occur.

For a given material, there is an equilibrium distance of the pair of atoms, at which the potential has a minimum. This distance is equivalent to the lattice constant (\( a_a \) or \( a_s \)) in a relaxed crystalline solid. The interaction will be attractive when distance between the pair of atoms is larger than the equilibrium distance; while it turns to be repulsive when the separation is smaller than it.

When adsorbate particles are deposited onto substrate, lattice constant is close to \( a_s \). In order to decrease the total energy adsorbate material try to achieve their favorite lattice constant \( a_s \). Relative distance is changed and atoms are shifted closer to or farther from their equilibrium positions.

Researches proved that strain can enhance the energy barrier as well as reduce it, depending on material property. Compressive and tensile strains contribute different to the binding energy because of the sign. This will lead to nucleate island or flat the surface.

Strain effect on adatom diffusion is studied. In ref.42, the change of diffusion kinetics is discussed by using a two-body Lennard-Jones potential. Diffusion is faster in the middle of the island for negative misfit compared to the island edge. However, positive misfit slows diffusion down in the middle of the island. Moreover, detachment barriers for atoms from steps are always reduced for strained layers. For negative misfit
this leads to a diffusion current from the island center towards the edges. This can e.g. result in a flat surface. On the other hand in the case of positive misfit the diffusion is to the island center and next layer nucleation can be enhanced.

Nevertheless, strain also affects the diffusion barriers on step edges, like hopping diffusion and exchange diffusion discussed above. As discussed before, the barrier for the downward movement plays an important role for the growth mode. High barriers lead to rough growth, whereas a low barrier leads to smoother layers at a given temperature. In Florian Much’s work (ref.41), the influence of the misfit on the diffusion barriers across steps has been investigated. The barrier for exchange diffusion moves down an island edge strongly depends on island size and misfit. The barrier decreases with increasing misfit and increasing island size. In the large misfit regime the barrier for exchange diffusion becomes smaller than de barrier for hopping diffusion.

Two general approaches are often used for the calculation of the elastic strain connected with self-assembled islands, namely, continuum elasticity and atomistic simulations.35 In the former method, the actual structure is replaced by an elastic continuum and the strain distribution is obtained by solving the elasticity equilibrium equation36,37 or by minimizing the elastic energy stored in the sample.38-40 In the atomistic simulation methods, two- and many- atoms potential are used for the calculation of the elastic energy of a sample; the strain is obtained by minimizing this energy.41,42
2.1.4 Growth mode

The spontaneous formation of 3D islands in strained-layer heteroepitaxy has recently emerged as a new technique for the synthesis of self-organized QDs.\textsuperscript{32–34} This technique is based on the fundamental morphological instability of strained surfaces, which is driven by the elastic relaxation of strain energy in the freestanding islands that spontaneously nucleate on the surface of a growing epitaxial layer after the completion of the wetting layer. The knowledge of the elastic strain field is important for understanding the mechanisms of dot formation, position correlation and creation of an equilibrium dot shape.

If a material is deposited on another one it is not clear in which way the growth will occur and what structure will form. Research results show us that it depends on the material properties such as lattice constant, crystal structure and so on, and also on the external conditions like temperature, pressure, etc.
Figure 2.5 Three growth modes in heteroepitaxial growth. (a) Frank-Van der Merwe growth mode, (b) Stranski-Krastanov growth mode, (c) Volmer-Weber growth mode.

So far, three popular growth modes are observed. They are Frank-Van der Merwe growth mode, Stranski-Krastanov growth mode, and Volmer-Weber growth mode. For elastic deformation, the growth mode occurred depends on the relative magnitudes of the surface energies, interfacial energy, and bulk strain energy.

In Frank-Van der Merwe growth mode (figure 2.5 (a)), it yields the lattice matched system and grows under the simplest way where one complete monolayer grows after the other. In Stranski-Krastanov growth mode (figure 2.5 (b)), coherent 3D islands form on a wetting layer of coherently growing adsorbate. It is important to stress that this process even takes place without any further deposition of particles. It is also known as the spontaneous 2D – 3D transition which results in the formation of self-assembled
QDs$^{45,46}$. In the case of Volmer-Weber (figure 2.5 (c)) growth mode (ref. 48), 3D adsorbate islands form directly on the substrate where the base of islands is constrained.

2.2 Monte Carlo method

From micro to macro scope, many efforts have been done related to the simulation of QDs growth. From microscopic view, like MD, detail description of a microstate is necessary, and then transition from one microstate to another is simulated until the system gets to equilibrium. At any time $t$, the microstate of the system can be defined by specifying the instantaneous positions and momentum of all the particles in the system. The transition from one microstate to another is generated as a time sequence by Newton’s second law. This method gives a precise description of the self-organization process. However, it is restricted to the particular system the microscopic model has been designed for and the applicability to other systems is rather limited.

For macroscopic method, like continuum method, the model is set up by a small amount of parameters neglecting the detail of the process. This approach gives analysis results for a large category loosing the feature of particular system.

Monte Carlo method of modeling QDs growth combining the microscopic events and macroscopic parameters gives a good resolution for the problem. The basis of a Monte Carlo simulation is single particle events, modeling single atom motion under particular environment. The time evolution of Monte Carlo method is using a Markov chain.

Monte Carlo method is widely used in study of equilibrium system. General model and frame work are well developed. For further study of Monte Carlo method in
equilibrium system, see ref.49. To be convenient, the main idea of the Monte Carlo method applied in this work is summarized.

2.2.1 Binding energy

To study the out-of-equilibrium behavior, we need to know in which way energy varies between the states. From one state $\mu$ to $\nu$ (for example, when an adatom moves from one site to another shown in Figure 2.6), the system must pass through transition $\mu \rightarrow \nu$ depends on the energies of these intermediates. In fact there is an energy barrier when adatom jump from one site to another.

Actually if there is only a single adatom on top of the surface, it jumps infrequently from one site on the surface to another adjacent one. It will stay in the same site for relatively a long time before it makes a jump.

If an adatom is in a four-fold hollow site, for transition from state $\mu$ to $\nu$, the adatom has to jump from one site to its neighbor site.

![Figure 2.6 Illustration of surface diffusion on (001) surface.](image-url)
During this process it has to pass through a series intermediate states where it contacts with less surface atoms (see in Figure 2.6). Therefore the energy at the intermediate state is higher than at the well bonded site.

The higher energy is called energy barrier. Because of this energy barrier adatoms prefer to stay in the same place for a relatively long period. In this single adatom hopping procedure, the main effect is the binding energy to the surface.

![Figure 2.7 Illustration of many adatoms case.](image)

For many adatoms case, the interactions between adatoms can affect the energy barriers. The interaction between adatoms is always called binding energy to the neighbor.

It is a difficult task to calculate the energy barriers for adatom hopping exactly. Calculating of the energy barrier can be found using ab-initio method. The energy barrier used in our model will be discussed in section 2.3.

2.2.2 Hopping rate

As mentioned before, the motion of the adatom is the competition result of the kinetic and thermodynamic, and adatom will stay at the same position for relatively a long time before it makes a jump.
The hopping probability for an adatom making a jump from a site $i$ to a site $j$ is related to energy barrier, and can be calculated by Arrhenius law:

$$\frac{r_{ij}}{k_B} = \nu e^{-\beta B_{ij}}$$  \hspace{1cm} (2.2a)$$

$$p = \nu_0 \exp\left(-\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (2.2b)$$

where $B_{ij}$ is the energy barrier for hopping from a site $i$ to a site $j$, which is significantly greater than the thermal energy $k_B T$ available for crossing it. $E_a$ is activation energy, which has the same value as energy barrier $B_{ij}$. The quantity $\nu$ is called the attempt frequency and set the overall time-scale for the movement of adatoms. From equation 2.2 we can see hopping rate decreases exponentially with increasing height of the energy barrier.

2.2.3 Monte Carlo algorithm

In our work, the crystal structure is simplified to be cubic; therefore the lattice is four-fold hollow site (refer to Figure 2.6). For the simplest case of just a single isolated adatom on a cubic lattice, the motion of adatom can be simulated according to the Arrhenius law. First choose a direction for adatom to hop in, and then make this move with an acceptance probability of $A = e^{-\beta B_{ij}}$. If this value is larger than the critical value, then the move will be accepted, or it will be rejected. Under this algorithm, each Monte Carlo step would be equivalent to an interval of real time $\Delta t = 1/4\nu$. The factor of four comes from the four directions in which the adatom can hop.
Figure 2.8 Energy barrier in one transition.

For many adatoms system, the same algorithm can be used. The difference is the calculation of binding energy, and to reject moves where already occupied by another atom.

2.3 Numerical model

In section 2.1 of this chapter, we discussed different adatoms motion and QDs growth mechanisms. Applying these theories into the numerical model, all the mechanisms turn out to be energy barriers encountered by adatoms during diffusion process in Monte Carlo method. Therefore, how to consider the energy barrier under different situation is the key issue in the QDs growth modeling. In this section, energy barriers under different environment is discussed and numerical model is also described. In our model, procedure of deposition, surface diffusion, interlayer diffusion, and misfit strain are considered.

Due to the steady growth of computer power they became an important tool for analyzing and understanding microscopic processes and their effects. During Monte Carlo method, energy barrier affect the motion of adatoms and morphology of surface.
Adatoms can diffuse on top of the surface in different manners. For example, in figure 2.9, (a) shows the deposition of an adatom; (b) desorption from surface; (c) can freely move in all directions; (d) can move along the step edge, diffuse around the kink site, jump to, or detach from the step; (e) can diffusion on top of the island or hop off it. For different diffusion modes the energy barrier adatoms have to conquer is different.

Theoretically, energy barrier for each move can be calculated by first-principle calculations,\textsuperscript{50–52} ab initio calculations\textsuperscript{53–55} or potential energy surface methods.\textsuperscript{56–58}

Potential energy surface method is a popular used method when calculate energy barrier and also simulate QDs growth. In this method, a test adatom moves in small steps on top of the crystal surface. The potential energy surface is obtained by using conjugate gradient method. Using this method, after each step the total potential energy is minimized by the variation of the coordinates of substrate atoms plus test atom coordinate perpendicular to the surface. Relaxation is stopped when both an energy convergence criterion is fulfilled and the largest force acting in the system is smaller than a certain upper bound. Potential energy and coordinates of the test atom then result in the
potential energy surface. Activation barriers for diffusion to a neighboring binding site are calculated using the conventional minimal energy path saddle-point method. Details of the method can be found in ref.59,60.

![Energy barriers diagram](image)

Figure 2.10 Energy barriers for an adatom diffusing on top of an island of a 2D surface.

Calculations carried by M. Schroeder and D. E. Wolf (ref.56) showed that the local relaxation or even frozen substrate give surprisingly accurate values for the energy barrier. Under this situation, only the objective adatom energies need to be recorded instead of measuring the total energy of the whole system. Since calculations for a frozen crystal save a lot of computer time and during the barrier calculations one only has to keep tracking of the adatom energies instead of the energy of the entire system, we restrict our method to the simplification of frozen crystal during the calculation of activation energy barrier. In the following, energy barriers calculation is carried on the frozen substrate. Practically, we can simplify the procedure.
2.3.1 Deposition barrier

From the vapor beam the adsorbate particles arrive at a random position on the surface of the crystal. In the initial motion of the particle is biased to energetically favorable sites with a high coordination number where the particle then sticks to the surface. After the deposition process has ended the particle is considered to be in a binding state.

In our work, we neglect the biased deposition, and simplify the process from energetically favorable sites to a random position. Therefore, after deposition the initial position of adatom is chosen randomly.

2.3.2 Surface diffusion barrier

After adatom arrives at the surface, it jumps laterally along the surface from one binding place to another. Because of the interaction of atoms, during diffusion adsorbate particles have to overcome binding energy, or the so called activation energy $E_a$.

$$E_a = E_s + E_n - E_{str}(x, y)$$  \quad (2.3)

As we mentioned in section 2.3.1, frozen model can give good result. Therefore, in flat surface diffusion, activation energy can be calculated by bound counting method. In equation (2.3), $E_s$ and $E_n$ are the binding energies to the surface and to the neighboring atoms, respectively. $E_{str}(x,y)$, a function of the plane coordinates $(x, y)$, which is the energy correction from the long-range strain field due to the lattice misfit between the substrate and the deposited material. We remark that, while the importance of strain for diffusion was addressed via first-principles calculation assuming a uniform axial or
biaxial strain field, with some interesting results for the strain induced diffusion and mobility features, the strain field and the corresponding strain energy are calculated using the Eshelby inclusion theory combined with the Green’s function solution.

The binding energy to the surface of the (x,y) plane, is also assumed to be constant, $E_s=1.3\,\text{eV}$, as in our previous 2D (x,y)-plane self-assembly model.$^{61,62}$

![Figure 2.11 Illustration of adatom and its neighbor positions.](image)

We calculate the binding energy to the neighboring atoms in the (x, y) plane, $E_n$, using the following approach. Moreover, as we assumed the model is set up on the frozen surface, we take the strength of all single nearest neighbor bonds $E_b$ to be 0.3 eV, and reduce it by a factor of $\alpha = 1/\sqrt{2}$ for the next nearest neighbors.$^{63,64}$ To evaluate the diffusion barrier, the binding energy at the site $P_0$, where the diffusing atom is located [one of the eight locations surrounding the center atom shown by the solid box in Figure 2.12]. It is calculated by

$$E_{P_0} = nE_b + m\alpha E_b$$

(2.4)

with $n \leq 4$ and $m \leq 4$ being, respectively, the number of nearest and next nearest atoms.

Similarly, for the site $P_1$ to which the atom is going to hop [one of the 16 locations surrounding the solid box shown by the dashed box in Figure 2.11], we have

$$E_{P_1} = g(nE_b + m\alpha E_b)$$

(2.5)
where \( n' \leq 4 \) and \( m' \leq 4 \) are, respectively, the number of nearest and next nearest atoms at the new site \( P_1 \), and \( g \) describes the coupling between the adjacent lattice sites. We point out that, while a small \( g \) corresponds to a weak coupling, a large \( g \) corresponds to a strong coupling. Following previous studies, we assume a weak coupling between the adjacent lattice sites with \( g=0.2 \). Therefore, the overall binding energy \( E_n \) caused by neighbor interactions for an atom to jump from site \( P_0 \) to site \( P_1 \) is given by the difference of the binding energies at the corresponding lattice sites,

\[
E_n = (n - gn')E_b + (m - gm')\alpha E_b
\]  

(2.6)

2.3.3 Interlayer diffusion barrier

As we mentioned in section 2.1, interlayer diffusion barrier helps to form the mount and roughness of the surface. In our model we use a variable ES barrier \( E_{ES} \) taking account for this over step hopping.

This barrier is caused by the reduced number of neighbors. It is only considered when adatom is going to make an interlayer jump at the step edge or island edge.

In this case the activate energy \( E_a \) turns out to be

\[
E_a = E_s + E_n + E_{ES} - E_{str}(x,y)
\]  

(2.7)

where \( E_{ES} \) stands for the ES barrier for interlayer hopping. Therefore this equation only happens when adatom make an over step hopping. Otherwise the surfaces diffusion should be considered as equation (2.3).
2.3.4 Strain energy calculation

As mentioned in previous sections, misfit induces large influence on energy barriers, QDs shape, surface patterning. Combining continuum elasticity theory of macroscopic solid instead of atomic interactions, the model is able to catch the important features in QDs growth.\textsuperscript{66,67} Though, for very small islands elasticity theory might give results different from atomistic calculations, for larger islands both theories should converge.\textsuperscript{68} Since the elastic equations are much simpler in evaluation effect of strain field, it is a good candidate for Monte Carlo simulation. In our model continuum mechanics is used to study the strain field.

For the strained semiconductor structure, strain energy should be calculated due to the point eigenstrain, instead of that due to the point/line force. Within the framework of continuum elasticity, the elastic strain induced by an island of atoms can be obtained using the Green’s function solution for the anisotropic semiconductor substrate. Details can be found in ref.36 and ref.37.

For a point (or concentrated) eigenstrain applied at point x, the induced elastic displacement and elastic strain can be expressed directly by the point-force Green’s functions without either volumetric or surface integration. Assuming that the point eigenstrain or point QD has an equal intensity of a sphere with radius $a$ (i.e., with a volume $V_a = \frac{4}{3}\pi a^3$) centered at x, then the QD-induced elastic strain fields are found to be,

\begin{equation}
\gamma_{kp} (y;x) = \frac{1}{2} \gamma^*_{lm} \left[ \sigma_{ml,p_y}^k (x,y) + \sigma_{ml,k_y}^p (x,y) \right]_a
\end{equation}

where the superscript k or p (=1, 2, 3) on the right-hand side of above equation indicates the direction of the point force, and the subscript prime followed by $p_y$ or $k_y$ in the stress
component $\sigma_{m1}$ denotes the derivative of Green’s stress. The strain energy at $y$ due to an island of atoms with area $A$ (with unit thickness in the out-of-plane $z$ direction) at variable $x$ can be calculated as

$$E_{str}(y) = \frac{1}{2} C_{ijkl} \int_{y} \gamma_{ij}(y;x) \gamma_{kl}(y;x) dA(x) \quad (2.9)$$

Discrete the consider area, the above equation can be simplified to

$$E_{str} = \frac{1}{2} C_{ijkl} \gamma_{ij} \gamma_{kl} A \quad (2.10)$$

where $C_{ijkl}$ is the elastic stiffness tensor. In the following calculation, it is assumed that the misfit strain is hydrostatic, i.e. $\gamma_{ij}^* = \gamma^* \delta_{ij}$ with $\gamma^* = 0.07$.

If surface strain energy caused by $(x, y)$ is denoted as $E_{str}(x, y)$, then strain energy which has the same $x$-coordinate and $y$-coordinate but different height to substrate surface is calculated as $E_{str}(x, y)e^{-h}$, where $h$ is the relative height to object point. That means

$$\begin{cases} E_{str}(x, y) & z_s = z_f \\ E_{str}(x, y)e^{-h} & otherwise \end{cases} \quad (2.11)$$

whereas $z$ stands for adatoms height to substrate.
CHAPTER III
QUANTUM DOT ISLAND DENSITY AND SIZE STUDY

3.1 Introduction

Self-assembled QDs have been intensively studied due to their unique optical and electronic properties, with potential applications in optoelectronics and semiconductor devices.\(^{69,70}\) The InAs/GaAs heterostructure is a typical example: it is characterized by a large lattice mismatch and undergoes a growth transition from a 2D layer to 3D islands.\(^{32,71}\) MBE offers the possibility of growing QD structures under well defined conditions. Mechanical shutters can interrupt the atomic beam efficiently so that deposit of less than one atomic layer becomes possible now.

Island size and density play an important role in the QD islands growth procedure. While controlling the size, density and spatial arrangement of InAs islands improves device characteristics, these factors are very sensitive to the growth conditions, such as coverage, flux rate, and temperature.\(^{72-76}\) Therefore investigation of QD island growth behavior under different growth conditions are necessary. Both experimental and numerical studies were carried out to investigate 3D InAs/GaAs QD island growth. Previous research showed that the islands size in early stage would affect their late growth. In particular, the critical diameter of QD islands was introduced to explain the phenomenon that different island diameters in early stage would lead to different growth
results. \(^{77}\) Islands would disappear after a period time of annealing if the islands are small at the early stage; however, the island size would continue to increase if its size is beyond certain critical diameter at the early stage. The InAs islands transition from 2D to 3D in their early stage is studied by Wu et al. who found that the islands density change experiences two periods with different increasing rates during the early stage of 3D growth.\(^{75}\)

In this chapter, we investigate the 3D InAs/GaAs QD island size and density evolution under different coverage and temperature by using our 3D KMC model. By comparing our simulation results to experimental ones, we found that there is a size limit for growth coverage. Below the limit existing islands can adsorb more new coming adatoms; however, beyond the limit new islands will be formed to adopt new coming adatoms. We also observed that with increasing temperature, the islands size will increase while their density will decrease.

3.2 Methodology

By applying the model described in the last chapter, we studied the island size and density distribution, where no dissolution is considered. The hopping probability of an atom from one lattice site to a nearest or next nearest neighbor is still governed by the Arrhenius law,

\[
p = n_0 \exp\left(-\frac{E_a}{k_BT}\right)
\]

Three aspects of active energy barriers are considered: binding energy to the surface \(E_s=0.1\text{eV}\), binding energy to the neighbor \(E_n\), Schwobel barrier \(E_{sch}=0.1\text{eV}\).
Binding energy to the neighbor is calculated depending on the local environment condition as discussed in the last chapter.

3.3 Coverage Effect

The effect of coverage on growth is investigated by changing the coverage values while keeping other growth parameters fixed.

First, three simulations are carried out to study the influence of coverage. The growth is under the temperature of 450°C, with a flux rate of 0.067ML/s, but with different coverage (Case A with 1.0ML, Case B with 1.6ML, and Case C with 2.0ML). Top views of growth results are shown in Figure 3.1. It is noticed that, with increasing interruption time, the QD island density decreases but the size of islands increases. This trend can also be observed experimentally as in ref.77. At the beginning of growth, adatoms quickly assembled together and formed many small islands. With increasing time, small islands join, and thus large islands are formed. In general, the film stress is compressive during the InAs island nucleation and growth; it then becomes tensile as the islands impinge upon one another, slowly becomes increasingly compressive as the continuous film thickens. Moreover, our results indicate that when the coverage is increased from 1.0ML to 2.0ML, more islands appear with increasing QD island density. New islands are formed to adopt new coming adatoms.
Figure 3.1 Top views of InAs/GaAs QD island growth results for different coverage. (A) with 1.0ML, (B) with 1.6ML, (C) with 2.0ML. The top row is the evolution process for Case A, the middle row for Case B, and the bottom row for Case C. The left column is the result for the system with self-organization for an interruption time of 100s, the mid-column is for 450s, and the right column is for 900s. Other fixed growth conditions are temperature 450°C and flux rate 0.067ML/s.
From the size distribution shown in Figure 3.2, we found that after the coverage reaches certain value, continuous increase of coverage will not increase the island size. More specifically, when the coverage increases from 1.0ML to 1.6ML, the QDs island density doesn’t change, but the average island size increases rapidly. However, when the coverage is further increased to 2.0ML, the average island size then decreases dramatically, while, the QDs density increases rapidly. In other words, when more adatoms arrive at the surface, instead of increasing islands size the system prefers to form more islands.
Figure 3.2 InAs/GaAs QD island size distribution after equilibrium (i.e. at the interruption time 900s). (a) Case A with $c=1.0\text{ML}$, (b) Case B with $c=1.6\text{ML}$, (c) Case C with $c=2.0\text{ML}$. The horizontal axis is the normalized island size, counted by the number of atoms inside the island, while the vertical axis shows the number of islands. Average QD island height (number of atoms in the vertical direction) is also shown at the top right corner. Other growth conditions are temperature at $450^\circ\text{C}$ and flux rate at $0.067\text{ML/s}$. 

average=270

average=421

average=352
Figure 3.3 InAs/GaAs QD island height distributions after equilibrium (i.e. at the interruption time 900s). (a) Case A with $c=1.0\text{ML}$, (b) Case B with $c=1.6\text{ML}$, (c) Case C with $c=2.0\text{ML}$. The horizontal axis is the island height in terms of lattice grid, and the vertical axis shows the number of islands. Average QDs height is shown at the top right corner. Other fixed growth conditions are temperature at $450\text{°C}$ and flux rate at $0.067\text{ML/s}$.
The relation between the islands number and island height is shown in Figure 3.3. It is observed that after the system reaches the equilibrium, an increase of the coverage will lead to an increase of the island height and the number of islands, but a decrease of the size of islands. Large islands loose atoms and small islands receive them so that the islands size in the system is equalized. Even new islands are formed to absorb new adatoms instead of increasing the size of the existing. Below the limit, islands will absorb new adatoms to increase their size; and once reaching the limit, new islands will form to receive new coming adatoms. While extra adatoms will help to grow in the vertical direction, the lateral dimension of the islands doesn’t change too much. In other words, islands are separated to each other at certain distance.

3.4 Temperature Effect

In order to compare the experimental results in ref.75, we have further studied the temperature influence on QD island size and density via our 3D KMC. InAs of 2ML is grown on top of the GaAs substrate with flux rate of 0.1ML/s. Temperature 500°C is applied to Case D, 530°C is applied to Case E, and 560°C is applied to Case F. The top views of the simulated results are shown in Figure 3.4. It is observed that, similar to Figure 3.1, small islands joined each other during the interruption process, thus, the number of islands is reduced after interruption. On observation of Figure 3.4, one could also notice that with increasing temperature fewer islands will be formed and so the QD island density is decreased. When temperature is increased, the QD island size increases. QD islands join each other to reduce the total energy.
Figure 3.4 Top views of the InAs/GaAs QD island growth results at different temperatures. (D) at 500°C (top row), (E) at 530°C (middle row), (F) at 560°C (bottom row). In each row, from left to right are results for interruption time 100s, 200s, and 500s, respectively. Other fixed growth parameters are flux rate of 0.1ML/s and coverage of 2ML.
Figure 3.5 InAs/GaAs QD island size distributions at interruption time 500s. (a) Case D (500°C), (b) Case E (530°C), (c) Case F (560°C). The horizontal axis is the normalized QDs size (in terms of number of atoms) and the vertical axis is the number of islands. Average QD island size is shown at the top right corner. Other fixed growth parameters are flux rate of 0.1ML/s and coverage of 2ML.
3.5 Results

In summary, QD island density and size distribution behavior is studied under different coverage and temperature conditions by using our 3D KMC model. By comparing our results to the experimental ones, we found that there is a QD island size limit for the growth coverage. Below this limit, existing islands become larger by adsorbing new coming adatoms; however, beyond the limit new islands will be formed to adopt new coming adatoms. Furthermore, when temperature is increased, larger islands are formed, and consequently, the QD island density is reduced.
4.1 Introduction

Self-assembled QD islands grown by Stranski-Krastanov mode are promising candidates for use in quantum devices because of their defect-free properties and ease of fabrication. However, physical properties are sensitive to the ordering on the surface. Thus, controlling lateral spacing and size distribution of the islands would enable improved device design.

Various methods have been proposed recently for patterning the substrate so that overgrown QD islands with uniform lateral ordering and equal size distribution can be achieved. Such control may be used to tailor the optoelectronic properties during synthesis and subsequently exploit correlation effects among dots. Techniques such as photolithography or nano-indentation are used to pattern the substrate. Surface modifications (using individual atoms, small clusters or generating mesas or holes) can act as nucleation sites, and their positions can be controlled with nanometer precision. Thus STM/AFM tips can be used to pattern the surface with a mesh of spatially ordered defects. Growth on such patterned surfaces is expected to lead to preferential island formation around the defects. However, lithographic patterning always introduces irregularities in the shape of the nanostructures, and mechanical damage to the interface.
cannot be avoided. The dots from lithographic techniques are also often too large and not with sufficient spatial density for device application. Therefore, the most promising quantum structures so far have been fabricated using techniques based on direct crystal growth. Strain-relief patterns are created spontaneously when a monolayer or two of one material is deposited on a substrate with a different lattice constant. It is also possible to directly confine the growth of InAs QD islands on a nanocavity array that is imprinted into the GaAs substrate surface via a highly ordered nanopore array template which is itself formed and self-organized in an anodic aluminum oxide (AAO) membrane. A brief review of various pre-patterning methods can be also found in ref.89.

Besides various fabrication approaches for pre-patterning on substrates, spatial ordering of QD islands on substrates can be achieved by vertical QD island stacking and by using high index substrates. It is particularly interesting that uniform spatial distributions of QD chains can be also obtained by adjusting the deposit material coverage and growth interruptions.

In this chapter, we present computer simulations for QD island self-organization on pre-patterned substrates where the pattern control is achieved by adjusting the growth interruption time. With consideration of the long-range elastic strain energy and under other fixed optimal growth parameters, spatial ordered QD island patterns are computationally predicted. Furthermore, correlation between the QD island pattern and substrate anisotropy (due to different crystalline orientations) can also be clearly observed.
4.2 Method

The hopping probability of an atom from one lattice site to a nearest or next nearest neighbor site in the (x,y)-plane is still governed by the Arrhenius law enhanced by the long-range strain energy field.\(^{96,97}\)

\[
p = v_0 \exp\left(-\frac{E_a}{k_BT}\right)
\]

\[
E_a = E_s + E_n + E_{ES} - E_{str}(x,y)
\]

In this case, the activate energy barrier contains four terms, besides terms about surface, neighbors, and step edge, strain energy is also considered. \(E_{str}(x,y)\) is the energy correction from the long-range strain field due to the lattice mismatch between the substrate and the deposited material. We remark that our model is multiscale-based where the continuum long-range strain is considered through the strain energy function in the atomistic KMC simulation. Computer modeling of QD island growth over pre-patterned substrates employing pure continuum mechanics was also reported recently.\(^{98,99}\)

4.3 Results

In simulating the effect of the growth interruption on the QD island distribution, three cases are studied: In Case 1, we deposit 1.6ML InAs atoms to the GaAs substrate and after that we give the system an interruption time of 250s (Figure 4.1); In Case 2, after depositing 0.3ML InAs atoms to the GaAs substrate, we stop and give the system 50s for interruption (Figure 4.2). After this interruption, we then deposit InAs atoms to this patterned substrate until the total coverage reaches 1.6ML. Finally, we let the system self-assemble for 200s (Figure 4.3), which gives a total interruption time 250s. In Case 3,
deposition of the InAs atoms to the GaAs substrate is interrupted for 50s at the end of
graduated coverages of 0.3ML, 0.6ML, 0.9ML, 1.2ML and 1.6ML (Figure 4.4). Therefore, the total interruption time is still 250s. To study the correlation between the QD island pattern and the substrate anisotropy, four different substrates are selected: Isotropic, GaAs (001), GaAs (111), and GaAs (113). We also remark that the InAs and GaAs atomic species are indistinguishable in our 3D KMC, but the different lattice constants and material properties between them are utilized in the long-range strain energy calculation.

Figure 4.1 shows, for Case 1, the QD islands distributed on a 100×100 grid over the isotropic substrate and the GaAs substrate with different crystalline orientations. The 1.6ML was deposited once without intermediate interruption. After the total deposition, the system is annealed for an interruption time \( t_i = 250s \). Other fixed growth parameters are temperature \( T = 800K \) and flux rate \( F = 0.1ML/s \). It is clearly observed from Figure 4.1 that, even though the long-range strain energy is included in the growth, the QD island spatial pattern is still very irregular.
Figure 4.1 InAs/GaAs QD islands distribution on a 100×100 grid with 1.6ML coverage. (a) Isotropic substrate, (b) GaAs (001) substrate, (c) GaAs (111) substrate, (d) GaAs (113) substrate. Left and right columns are, respectively, the top-down plan and 3D views. Other fixed growth parameters are temperature \( T = 800K \), flux rate \( F = 0.1\text{ML/s} \), and interruption time \( t_i = 250\text{s} \).
Figure 4.2 InAs/GaAs QD islands distribution on a 100×100 grid with 0.3ML coverage. (a) Isotropic substrate, (b) GaAs (001) substrate, (c) GaAs (111) substrate, (d) GaAs (113) substrate. Left and right columns are, respectively, the top-down plan and 3D views. Other fixed growth parameters are temperature $T=800$K, flux rate $F=0.1$ML/s, and interruption time $t_i=50$ s. This QD pattern is used for continuous deposition of atoms in Cases 2 and 3.
Figure 4.2 shows QD island distribution on a 100×100 grid over the isotropic substrate and the GaAs substrate with different crystalline orientations. Different to Figure 4.1, here only 0.3ML coverage is deposited and after the deposition, 50s is given for annealing. It is clearly observed that by depositing a certain small amount of the atoms to the substrate, well organized QD islands patterns can be achieved, with the latter being able to be used as pre-pattern for further deposition as we will show below for Cases 2 and 3.

Figure 4.3 shows, for Case 2, the QD islands distribution on a 100×100 grid over the isotropic substrate and the GaAs substrate with different crystalline orientations. Here, the pre-pattern obtained in Figure 4.2 is utilized for continuous deposition. In other words, after deposition of 0.3ML followed by 50s interruption, the remaining 1.3ML was deposited and the system is then annealed for 200s so that the total interruption time is still 250s. Comparing Figure 4.3 to 4.1, it is observed that introducing an intermediate interruption time during growth can help to achieve better QD island spatial ordering. This conclusion is similar to the recent experimental observation from Wang at al,92 and it is also consistent with other previous experimental and simulation results. It has been demonstrated that a growth interruption has a smoothing effect on crystal surface,100 and that after the growth interruption the system exhibits an ordered pattern.101 Therefore, it could be possible to control the QD island pattern by adjusting the growth interruption time.
Figure 4.3 InAs/GaAs QD islands distribution on a 100×100 grid with a total coverage of 1.6ML coverage, grown from the island pattern in Figure 4.2. (a) Isotropic substrate, (b) GaAs (001) substrate, (c) GaAs (111) substrate, (d) GaAs (113) substrate. Left and right columns are, respectively, the top-down plan and 3D views. Other fixed growth parameters are temperature $T=800\text{K}$, flux rate $F=0.1\text{ML/s}$, and interruption time $t_i=200\text{s}$ after the total coverage of 1.6ML. Therefore, total interruption time is 250s.
Figure 4.4 InAs/GaAs QD islands distribution on a 100×100 grid with a total coverage of 1.6ML. (a) Isotropic substrate, (b) GaAs (001) substrate, (c) GaAs (111) substrate, (d) GaAs (113) substrate. Left and right columns are, respectively, the strain energy distribution on the substrate and top-down plan view. Other fixed growth parameters are temperature $T=800$K and flux rate $F=0.1$ML/s. Deposition is interrupted for $t_i=50$s at the end of coverage of 0.3, 0.6, 0.9, 1.2, and 1.6ML. Therefore, the total interruption time is still 250s.
We show in Figure 4.4 the spatial distribution of the self-organized QD islands on different substrates for Case 3. Shown in the left column is the strain energy distribution on the surface of the substrate. The 3D KMC simulation is also on the 100×100 grid with fixed temperature $T=800\text{K}$ and flux rate $F=0.1\text{ML/s}$, as in Cases 1 and 2. However, the deposition is interrupted for 50s at the end of coverage of 0.3, 0.6, 0.9, 1.2, and 1.6ML, keeping the total interruption time at 250s. Comparing the QD islands spatial distribution in Figure 4.4 with those in Figures 4.3 and 4.1, we clearly observe that sharper spatial ordering of QD islands can be achieved with increasing intermediate interruption steps. Comparing the strain energy distribution in the left column with the QD islands growth patterns in the right column in Figure 4.4, we also notice a clear correlation between the growth pattern and substrate anisotropy (or orientation). This result is consistent with other recent reports.\textsuperscript{35}

The proposed pre-patterning approach can not only improve the spatial ordering of the QD islands, but also make the island-size more uniform. This is shown in Figure 4.5 where the histograms for the number of islands versus island size are presented.
Figure 4.5 Histograms of number of QD islands versus island size for InAs QD growth Cases 1 to 3 (columns left, middle, and right) on the isotropic, GaAs (001), GaAs (111), and GaAs (113) substrate (rows from top to bottom). The growth is on a 100×100 grid over the substrate with a total coverage of 1.6ML. Other fixed growth parameters are temperature $T=800\text{K}$ and flux rate $F=0.1\text{ML/s}$. Case 1 is without intermediate interruption; Case 2 is for an intermediate interruption of 50s after 0.3ML coverage; and Case 3 is for intermediate interruption time of 50s at the end of coverage of 0.3, 0.6, 0.9, 1.2, and 1.6ML.

4.4 Conclusion

Utilizing a recently proposed 3D KMC algorithm for 3D QD self-assembled growth, we simulated the corresponding QD island growth on pre-patterned substrates,
where the pre-pattern is actually the pre-grown atom islands on the substrate. By introducing the intermediate interruption time during growth, QD islands with more uniform size and shaper spatial ordered islands can be achieved. The correlation between the QD spatial pattern and substrate anisotropy (orientation) can also be clearly observed. Our results suggest that in MBE growth of QDs islands, intermediate interruption times can be introduced. This experimentally specifiable parameter could enable an additional means of controlling 3D QD island array uniformity.
CHAPTER V
FUTURE WORK

In previous chapters, we introduced our 3D model used for QDs growth. Several important factors have been discussed. First, using this numerical model QDs islands size and density distributions influenced by coverage and temperature are studied according to different experimental conditions. Furthermore, numerical simulation is done for pre-patterned QDs growth.

However, the model used in this work is a much simplified one. First of all, crystal structure is simplified to cubic one. Second, deposition process should be an energetically favorable position, but not the random site we used in this work. Third, diffusion length is set to one grid where in the real case it depends on the environment detail. Forth, several mechanisms has been ignored such as exchange diffusion at step edges and dimer movement. Therefore, in the future study to provide more accurate analysis results, it is better to improve the model to reduce the number of assumptions.

In this work, we studied the QDs formation and growth which is a process of gathering adatoms. There is another very important application of nanostructures which is an opposite procedure called lamina growth. It is an important structure in real applications. In this growth where cluster nuclear is not wanted, on the contrast the flat surface with several layers thickness is needed.
REFERENCES


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