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The Hong Kong Polytechnic University Department of Applied Physics

A Layer-by-layer Growth Mechanism

for Three-dimensional Island Nucleation

in Strained Heteroepitaxy

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Philosophy

August 2008

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Abstract

A theoretic model of layer-by-layer growth for heteroepitaxial films is introduced in this thesis, in order to explain the morphological evolution of strained heteroepitaxial films. The energetics related to island formation are analyzed. There are two main energy terms which contribute to the total free energy for the whole system: strain energy and island step free energy. We have investigated two-dimensional (2D) circular single layer islands and stacked three-dimensional (3D) circular islands with n layers ($n \ge 2$). The island strain energy is calculated by using a small-slop approximation, and the step free energy is calculated by using a ball and spring model. Moreover, we have considered the entropic repulsion between two adjacent steps.

This model can explain the following observations from simulation results using kinetic Monte Carlo method under slow deposition conditions. At the early stage of a deposition process, only 2D islands exist. Next, 3D island formation follows a layer-by-layer growth mode. Only if an n-layer island grows laterally larger can a new layer of atoms nucleate on top. There is an equilibrium shape for an n-layer island: the separation between the steps at adjacent layer decreases when the number of layers of the island increases accompanying deposition. Good agreement is found between the model and the Kinetic Monte Carlo simulation results.

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Chapter 1

Introduction

Nature is beautiful and amazing, for it provides us with various patterns and shapes, varying from star galaxies in large scales, to objects in micro scales such as shapes of plant leaves, ridges of our fingerprints which can be seen with our naked eyes and shapes of the little snowflakes in the cold winter captured by optical microscope. It is human being's interest to explore the mysteries of how these patterns are formed. Since 1960s, fast development of microscope techniques, such as scanning tunneling microscopy (STM), atomic force microscopy (AFM) and transmission electron microscopy (TEM), allow us to "see" the details of the atomic world which are also very fantastic. The reliable and highly accurate microscopes can provide us the profile of the crystal surface in nanoscales, which can be very useful, for example, to characterize surface roughness, observe surface defects, etc. From the observations of the atomic structure of crystal surfaces by STM, coherently strained islands in heteroepitaxial growth attract much interest [1,2]. Under appropriate growth condition, self-assembled islands are observed in heteroepitaxial system including Ge/Si, InAs/GaAs, InAs/InP, etc, and they are considered to be of potential use in manufacturing nanoelectronic devices. It is also an important and interesting topic to understand the mechanism of how these islands form.

1.1 Overview

Epitaxy is a kind of crystal growth which refers to the method of depositing monocrystalline film on a monocrystalline substrate. It can be divided into two categories: homoepitaxy growth and heteroepitaxy. Homoepitaxy is a kind of epitaxy in which the materials of the substrates and films are the same, while heteroepitaxial growth refers to growth in which the materials of substrates and films are different from each other. Heteroepitaxy has attracted much research



Figure 1.1: Heteroepitaxy of lattice-mismatched materials. Top shows the lattice difference between the film material and the substrate material; bottom shows that the film materials are strained on the surface of the substrate.

interest recently because the mechanism is much more complex than that of homoepitaxy. In a heteroepitaxial system, the lattice constants between the two different materials are in general different, hence the film in a heterogrowth system is intrinsically stressed. The lattice misfit is defined as

$$\varepsilon = \frac{a_f - a_s}{a_s} \tag{1.1}$$

where a_f is the lattice constant of the film and a_s is the lattice constant of the substrate (as shown in Fig. 1.1). Strain and stain relaxation play a very important

role in heteroepitaxy.



Figure 1.2: Schematic diagram of the three growth modes: Frank-Van der Merwe (FM), Volmer-Weber (VW), Stranski-Krastanov (SK).

There are basically three modes for crystal growth as shown in Fig. 1.2: Volmer-Weber (VW) [3], Frank-Van der Merwe (FM) [4], and Stranski-Krastanov (SK) [5]. In Volmer-Weber growth, small nuclei form and grow into three dimensional islands with out a wetting layer. In Frank-van der Merwe growth, the film processes a two-dimensional (2D) layer-by-layer growth mode. Stranski-Krastanov growth is an intermediary process which starts initially with layer to layer growth, and then follows by 3D island formation.

One of the most widely studied systems is the Ge/Si heteroepitaxial system, in which pure Ge islands or $Ge_{1-x}Si_x$ alloy islands form following the SK growth mode. Ge wets Si surface and performs a layer-by-layer growth first up to a critical film thickness first. The mismatch in lattice constant between Ge and Si is about 4%. In a low temperature regime ($T < 550^{\circ}C$), when Ge is deposited on Si surface, it is believed that only pure Ge islands are observed, and Ge alloying with Si does not take place. Rectangular hut Ge islands on Si substrate in ridge and pyramid geometries were reported [6–9]. These islands are bonded by (105) facets and they are the smallest observed islands which are best suited for nanometer sized application. If the substrate temperature is high ($T > 550^{\circ}$ C), Ge_{1-x}Si_x alloy islands would be observed due to the interdiffusion at Ge/Si interface. In 2003, P. Sutter and his coworkers have reported the continuous formation



Figure 1.3: STM images in Ref. [10]. (a) STM image of 40 ML $Ge_{0.75}Si_{0.25}$ grown on Si (100). (b) Shallow mound marked in (a). (c) A tall mound marked in (a). (d) Surface profiles along the [001]/[011] lines in (c).

and faceting of GeSi alloy islands [10]. The STM images of their experiment on $Ge_{0.75}Si_{0.25}/Si$ at 40 monolayers nominal alloy coverage show the islands at a very early stage. Shallow mounds occur and the angles of the side wall are about 1°-3° at first. The mounds which are in a wedding-cake-like shape consist of (100) terraces separated by atomic steps. As the deposition process continues, the angles of the side wall of the shallow mounds start to increase until about 11°, and shallow mounds turn into hut islands with the characterizing (105) facets.

1.2 Motivation and objectives

To better understand the surface roughening process in heteroepitaxy, Lung and Lam have proposed a Kinetic Monte Carlo (KMC) model in three dimensions [11]. The KMC simulation model will be presented in section 2.4 of Chapter 2. In Ref. [11], they have reported a sequential layer-by-layer mechanism for a growing island or pit. However, the theoretical analysis is lacking. To further study the mechanism, by using the same model, 11 independent runs under low rate deposition condition below roughening temperature have been perform. The primary objective of this thesis is, based on the analysis of energetics for islands under strain, to set up a model for the initial stage of crystal growth to better understand about the mechanism related to the evolution of the surface morphology in heteroepitaxy, especially the sequential layer-by-layer growth mechanism.

Chapter 2

Theoretical models

This chapter will first introduce the energetics related to heteroepitaxial growth in section 2.1. Then, three research methodologies which are intensively used are introduced. The first one is the continuum model and will be introduced in section 2.2. The second one is the a ball and spring model and will be presented in section 2.3. The last one is the Kinetic Monte Carlo simulation which is based on the ball and spring model, and will be introduced in section 2.4.

2.1 Energetics of strained heteroepitaxial islands

We start this chapter by introducing the competing energies for a single coherent island. For a *dilute* system, the interaction between islands can be neglected. Hence we need only calculate the energy of a single island. The competing energies include the elastic energy and the surface energy. Hence, the total free energy E_{total} for a single island is given by:

$$E_{total} = E_{elastic} + E_{surf} \tag{2.1}$$

The first term $E_{elastic}$ in Eq. (2.1) refers to the energy due to the elastic



compression. Figure 2.1 shows schematic diagrams for the substrate and the

Figure 2.1: Schematic diagrams of strain relaxation during heteroepitaxial growth. White areas in the two graphs denote the substrate, and grey areas denote the film. The diagram on the left represents an unrelaxed state and the right diagram represents a relaxed state.

film in two states. The diagram on the left in Fig. 2.1 shows that the film is uniformly strained on the substrate, with unphysical external stresses which keep the system in the unrelaxed state. Without these external stresses, the system will be in a relaxed state, as shown in the right diagram of Fig. 2.1. We have

$$E_{elastic} = E_{homo} + \Delta E_{relax} \tag{2.2}$$

where, E_{homo} is the bulk homogeneous strain energy, referring to the strain energy when the substrate and film are in the unrelaxed state. It is proportional to the number of the atoms in the film. The bulk homogeneous strain energy per film atom E_s^0 will be calculated in section 3.4. The next term ΔE_{relax} is the change of the strain energy due to the elastic relaxation, i. e. the strain energy difference between system in the unrelaxed state and in the relaxed state.

The second term E_{surf} in Eq. (2.1) is the change of the surface energy due to changes in surface area and orientation during formation of the island. In this thesis, we consider that an inclined surface consists of steps. Hence, E_{surf} is proportional to the length of the steps and the step free energy per edge length. We define E_{strain} to be ΔE_{relax} for the elastic energy relaxation for an island, as it is commonly used in many literature.

2.2 Continuum elasticity model

To evaluate the strain relaxation energy for island formation, we use a continuum elastic model. In the continuum model, we treat the system as a continuum elastic solid. The substrate and the deposited material are assumed to have the same elastic constants for simplicity. Tangential elastic forces at the steps are assumed to be applied on the flat surface of the substrate. We use a small-slope approximation. It is a good assumption when surface roughness is small.

The displacement in response to the surface elastic force $f_j(\mathbf{r})$ can be written by [12]

$$u_i(\boldsymbol{r}) = \int d\boldsymbol{r}' G_{ij}(\boldsymbol{r} - \boldsymbol{r}') f_j(\boldsymbol{r}')$$
(2.3)

where $u_i(\mathbf{r})$ is the displacement of the film in *i*th direction on the surface, and G_{ij} is the half-space elastic Green's function, which depends only on the material properties. By using elastic Green's Function, the strain energy relaxation E_{strain} can be written as

$$E_{strain} = -\frac{1}{2} \sum_{i,j} \int d\mathbf{r} d\mathbf{r}' G_{ij}(\mathbf{r} - \mathbf{r}') f_i(\mathbf{r}) f_j(\mathbf{r}')$$
(2.4)

2.3 Ball and spring lattice model

In a Ball and spring model, atoms of the film and the substrate are represented by balls on a cubic lattice and they are connected by springs, which represent the bonds between the atoms. We consider only the nearest neighbor (NN) and the next nearest neighbor (NNN) interactions. There are 6 nearest bonds and 12 next nearest bonds for each bulk atom. The Kinetic Monte Carlo (KMC) simulations discussed in section 2.4 are based on the ball and spring model. The step energy of the island presented in Chapter 3 is also based on this model.

2.4 Kinetic Monte Carlo simulations

In this section, we introduce the Kinetic Monte Carlo simulation model proposed by Lung and Lam [11]. The model is based on a ball and spring model of cubic lattice. Efficient algorithms are used which allow to simulate the morphologies under a much wider range of conditions. The morphological evolution is achieved by considering adatom hopping. Surface diffusion is simulated by hoppings of the topmost atoms in the film, and hoped atom will be deposited at a random site nearby.

The hopping rate Γ_m of a topmost atom m is given by

$$\Gamma_m = R_0 \exp(-\frac{n_{m,NN}\gamma_{NN} + n_{m,NNN}\gamma_{NNN} + \Delta E_m + E_0}{k_B T}) \qquad (2.5)$$

where R_0 is the rate constant related to the diffusion coefficient. The term $n_{m,NN}\gamma_{NN} + n_{m,NN}\gamma_{NNN}$ is the energy needed to break the chemical bonds around the *m*th atom. The term ΔE_m is the the difference in elastic energy of the whole lattice when the site *m* is occupied versus unoccupied. The last term E_0 is an energy barrier offset.

Next, we present the Kinetic Monte Carlo simulations carried out by Lung, Xiang and Lam [13], which we will analyze with the same algorithms. The lattice constant for the substrate is assumed to be $a_s = 2.715$ Å, which gives the right atomic volume in crystalline silicon. The bond strength for atoms to connect to its nearest neighbors γ_{NN} and to its next nearest neighbors γ_{NNN} are chosen to be

$$\gamma_{NN} = 0.085 \,\mathrm{eV} \tag{2.6}$$

$$\gamma_{NNN} = \frac{\gamma_{NN}}{2} \tag{2.7}$$

The force constants of the elastic springs are taken as $k_{NN} = 2eV/a_s^2$ and $k_{NNN} = k_{NN}$ respectively. The surface for our system is a (100) surface which contains 32×32 atoms. Depositions of films with 8% lattice mismatch have been simulated at 600K at low deposition rates. It is believed that 600K is below the roughening temperature, and no alloying process exists in a Ge/Si heteroepitaxial system. We will analyze 11 independent simulations with different deposition rates, including $1ML s^{-1}$, $3ML s^{-1}$ and $10ML s^{-1}$. The simulation results will be presented in section 6.1 of Chapter 6.

Chapter 3

Energetics for strained heteroepitaxy

In this chapter, we will first explain the calculation for surface step energy in section 3.1 and entropic step repulsion in section 3.2. Then, some basic strain-related calculations are given, including elastic force in section 3.3, homogeneous bulk strain energy per atom E_s^0 in section 3.4 and the half-space Green's function in section 3.5.

3.1 Step free energy

To obtain the step free energy of a monolayer step, we start from considering a step in the [100] direction on the (001) surface [14]. By counting the



Figure 3.1: Schematic diagrams for a [100] step (left) and a [110] step (right) on (100) surface.

number of broken bonds per step-edge atom based on the ball and spring model, we can get the step formation energy in the [100] direction. For each atom on the edge, one nearest neighboring bond and two next nearest neighboring bonds need to be broken, so the step energy in the [100] directions $E_{[100]}$ is given by

$$E_{[100]} = \frac{\gamma_{NN}}{2} + \gamma_{NNN} \tag{3.1}$$

Let $E_{kink}(n)$ be the formation energy for a kink in which an otherwise straight



Figure 3.2: Schematic diagrams for a kink with transverse displacement a_s at [100] step on (100) surface.

surface step is displaced transversely by na_s . For such a kink in a [100] step, n more nearest neighboring bonds and (n - 1) more next nearest neighboring bonds need to be broken. Hence $E_{kink}(n)$ and is given by

$$E_{kink}(n) = n\frac{\gamma_{NN}}{2} + (n-1)\gamma_{NNN}$$
(3.2)

The partition function of a [100] step $Z_{[100]}$ is then

$$Z_{[100]} = e^{-(\frac{\gamma_{NN}}{2} + \gamma_{NNN})/k_BT} \left(1 + 2\sum_{n=1}^{\infty} e^{-[n\frac{\gamma_{NN}}{2} + (n-1)\gamma_{NNN}]/k_BT} \right)$$
(3.3)

The step free energy $F_{[100]}$ is given by

$$F_{[100]} = -k_B T \ln(Z_{[100]})$$

$$= \frac{\gamma_{NN}}{2} + \gamma_{NNN} - k_B T \ln \left[1 + \frac{2e^{-(\frac{\gamma_{NN}}{2} + \gamma_{NNN})/k_B T}}{1 - e^{-(\frac{\gamma_{NN}}{2} + \gamma_{NNN})/k_B T}} \right]$$
(3.4)

where the second term in Eq. 3.4 is related to the entropy for the step. In the simulation, $\gamma_{NN} = 0.085 \text{eV} = 2\gamma_{NNN}$. So the step free energy per length

equals

$$\sigma = \frac{1}{a_s} F_{[100]} \tag{3.5}$$

Fig. 3.3 shows the temperature dependence of σ in [100] direction. The step



Figure 3.3: Step free energy per unit length σ versus temperature T.

energy vanishes at T_r =1175.34K.

For a surface step in [110] direction, there are two nearest neighboring bonds and two next nearest neighboring bonds which needs to be broken. The step length per atomic unit equals $\sqrt{2}a_s$, so

$$E_{[110]} = \frac{\sqrt{2}\gamma_{NN}}{2} + \frac{\sqrt{2}\gamma_{NNN}}{2}$$
(3.6)

We should point out that the difference between $E_{[100]}$ and $E_{[110]}$ is only 6%. Hence, for simplicity, we only use the result for step in [100] direction. The value of the step free energy per unit length we use in this thesis is $\sigma =$ 0.0192592eV/atom, which is the step free energy for [100] step at T = 600K.

3.2 Entropic step repulsion

Besides the free energy for a single step, we also consider the entropic step repulsion for two adjacent steps. The origin of entropic step repulsion is that when two steps get too close, the entropy of each step is reduced [15]. The entropy related to step repulsion was first calculated by Gruber and Mullins [16]. They showed theoretically that the configurational entropy of a step trapped between two walls of separation 2w is given by

$$S(T,w) = S_0(T) - g'(T)/w^2$$
(3.7)

where S_0 is the entropy of a free step without walls and g' is a width-independent constant. In our case, when $w = a_s$, the entropy S = 0. So g'(T) equals

$$g'(T) = S_0 a_s^2 (3.8)$$

Using also Eq. 3.4, S_0 is given by

$$S_0 = k_B \ln \left[1 + \frac{2e^{-(\frac{\gamma_{NN}}{2} + \gamma_{NNN})/k_B T}}{1 - e^{-(\frac{\gamma_{NN}}{2} + \gamma_{NNN})/k_B T}} \right]$$
(3.9)

Therefore, with step repulsion, the step energy per edge-atom becomes

$$\sigma_{step} = \sigma + \tilde{\sigma} \tag{3.10}$$

where $\tilde{\sigma}$ is given by

$$\tilde{\sigma} = Tg'(T)/a_s/w^2 = k_B T \ln \left[1 + \frac{2e^{-(\frac{\gamma_{NN}}{2} + \gamma_{NNN})/k_B T}}{1 - e^{-(\frac{\gamma_{NN}}{2} + \gamma_{NNN})/k_B T}} \right] a_s/w^2$$
(3.11)



Figure 3.4: Step energy per unit length σ_{step} which consider the entropic repulsion versus step separation w at T=600K (solid line). The dashed line is the step free energy without repulsion σ .

Fig. 3.4 shows the step energy with repulsion σ_{step} versus the step separation w. In particular, when $w = a_s$, $\sigma_{step} = 0.03125 \text{eV/Å}$. When $w \to \infty$, $\sigma_{step} = 0.0192592 \text{eV/Å}$.

3.3 Elastic force

The distribution of surface elastic force in Eq. (2.4), which is induced at the surface where the surface stress varies, can be calculated by [17]

$$f_i(\boldsymbol{r}) = \nabla_j \sigma_{ij}(\boldsymbol{r}) \tag{3.12}$$

Here, σ_{ij} is a stress tensor given by

$$\sigma_{ij} = \sigma_b h(\boldsymbol{r}) \delta_{ij} \tag{3.13}$$

$$\delta_{ij} = \begin{cases} 1, & i=j, \\ 0, & i \neq j. \end{cases}$$
(3.14)

where δ_{ij} is the Kronecker delta, and $h(\mathbf{r})$ is the height (thickness) of the island at position \mathbf{r} . The term σ_b is the xx or yy component bulk stress of island uniformly strained to the substrate x and y lattice constants. It is given by

$$\sigma_b = \frac{E_{film}}{1 - \nu} \varepsilon \tag{3.15}$$

where E_{film} and ν are two elastic constant referring to the Young's modulus and the poisson's ratio respectively, and ε is the lattice mismatch between the film and the substrate. The elastic force $f_i(\mathbf{r})$ is simplified by using

$$f_i(\boldsymbol{r}) = \sigma_b \partial_i h(\boldsymbol{r}) \tag{3.16}$$

For a flat surface with $h(\mathbf{r}) = 0$, it is free of net surface elastic force. For an island facet with an inclination angle θ , the force per unit area f_a equals

$$f_a = \frac{E_{film}}{1 - \nu} \varepsilon \tan \theta \tag{3.17}$$

For a 2D island, the force per unit length on the island edge f_l equals

$$f_l = \frac{E_{film}}{1 - \nu} \varepsilon a_s \tag{3.18}$$

From the ball and spring model, it can be shown that the elastic constant E_{film} and ν can be calculated by

$$E_{film} = \frac{k_n^2 + 5k_nk_{nn} + 4k_{nn}^2}{a_s(k_n + 3k_{nn})}$$
(3.19)

$$\nu = \frac{k_{nn}}{k_n + 3k_{nn}} \tag{3.20}$$

3.4 Homogeneous strain energy per atom E_s^0

The general expression for the free energy of a deformed isotropic body is [18]

$$F = F_0 + \frac{1}{2}\lambda u_{ii}^2 + \mu u_{ik}^2 \tag{3.21}$$

Hence, the homogeneous strain energy per atom E_s^0 can be calculated by

$$E_s^0 = \left(\frac{\lambda}{2}(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})^2 + \mu(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2) + 2\mu(\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{zx}^2)\right)a_s^3$$
(3.22)

where

$$\varepsilon_{xx} = \varepsilon$$
 (3.23)

$$\varepsilon_{yy} = \varepsilon$$
 (3.24)

$$\varepsilon_{zz} = -\frac{2\lambda\varepsilon}{\lambda+\mu}$$
 (3.25)

and

$$\varepsilon_{xy} = \varepsilon_{xz} = \varepsilon_{yz} = 0 \tag{3.26}$$

Here, λ and μ are called Lamé coefficients. They are given by

$$\lambda = \frac{E_{film}\nu}{(1+\nu)(1-2\nu)} \tag{3.27}$$

$$\mu = \frac{E_{film}}{2(1+\nu)} \tag{3.28}$$

Therefore,

$$E_s^0 = \frac{E_{film}\varepsilon^2}{1-\nu}a_s^3 \tag{3.29}$$

3.5 The half-space Green's function

The Green's function for an elastic media, which plays an important role in the application of linear elasticity, is defined to be the relationship between force and the responsive displacement. It can be obtained by finding the fundamental point force solutions, for example, the point force solutions for a full space by Kelvin, solutions for point force on the surface of a half space by Boussinesq and Cerruti and the solutions for a point force buried in a half space by Mindlin, etc. The displacement field for a given force distribution is then the integration of a point force solution around the region of the applied force.

To obtain the half-space Green's function, we start from the displacement for point force on the bounded surface of a half-space. Considering an isotropic half space z < 0, the displacement field due to a point force F applied at (x, y, z) = (0, 0, 0) on the surface of the medium is given by [18]

$$u_{x} = \frac{1+\nu}{2\pi E_{film}} \cdot \frac{1}{r} \left\{ -\frac{(1-2\nu)x}{r} F_{z} + 2(1-\nu)F_{x} + \frac{2\nu x}{r^{2}} (xF_{x} + yF_{y}) \right\} (3.30)$$

$$u_{y} = \frac{1+\nu}{2\pi E_{film}} \cdot \frac{1}{r} \left\{ -\frac{(1-2\nu)y}{r} F_{z} + 2(1-\nu)F_{y} + \frac{2\nu y}{r^{2}} (xF_{x} + yF_{y}) \right\} (3.31)$$

$$u_{z} = \frac{1+\nu}{2\pi E_{film}} \cdot \frac{1}{r} \left\{ 2(1-\nu)F_{z} + (1-2\nu)\frac{1}{r} (xF_{x} + yF_{y}) \right\} (3.32)$$

where $\boldsymbol{u} = (u_x, u_y, u_z)$ is the displacement vector.

For a tangential point force, $F_z = 0$. The displacement u(r) on the surface (z = 0) can be written in a compact form [19]

$$\boldsymbol{u}(\boldsymbol{r})\Big|_{\boldsymbol{z}=\boldsymbol{0}} = \frac{1-\nu^2}{\pi E_{film}} \cdot \frac{1}{r} \boldsymbol{F} + \frac{\nu(1+\nu)}{\pi E_{film}} \frac{\boldsymbol{r}}{r^3} (\boldsymbol{F} \cdot \boldsymbol{r})$$
(3.33)

Generalizing to a tangential force distribution f(r) on the surface, using

Eq. (3.33) and Eq. (2.4), we get

$$E_{strain} = -\frac{1}{2} \iint \left(\frac{1-\nu^2}{\pi E_{film}} \frac{\boldsymbol{f}(\boldsymbol{r}) \cdot \boldsymbol{f}'(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\nu(1+\nu)}{\pi E_{film}} \frac{\boldsymbol{f}(\boldsymbol{r}) \cdot (\boldsymbol{r}-\boldsymbol{r}') \boldsymbol{f}'(\boldsymbol{r}') \cdot (\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3} \right) d\boldsymbol{r} d\boldsymbol{r}'$$

$$(3.34)$$

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Chapter 4

Energetics for axisymmetric islands

In this chapter, we will present strain energy calculations for 2D island in section 4.1, cylindrical n-layer island in section 4.2 and general circular n-layer island in section 4.4. Then, the calculation for total energy change when forming an island and the chemical potential are described in section 4.5, and section 4.6 respectively.

4.1 2D circular island

Consider a circular island of radius r, the strain relaxation energy $E_{strain}^{1}(r)$ can be calculated by integrating Eq. (3.34) around its circular boundary [19], as shown in Fig. 4.1. Then $E_{strain}^{1}(r)$ is given by

$$E_{strain}^{1}(r) = -\frac{1+\nu}{2\pi E_{film}} \oint \oint \left(\frac{1-\nu}{|\mathbf{r_{1}}-\mathbf{r_{2}}|} \mathbf{f}_{1} \cdot \mathbf{f}_{2} + \nu \frac{\mathbf{f}_{1} \cdot (\mathbf{r_{1}}-\mathbf{r_{2}}) \mathbf{f}_{2} \cdot (\mathbf{r_{1}}-\mathbf{r_{2}})}{|\mathbf{r_{1}}-\mathbf{r_{2}}|^{3}} \right) ds_{1} ds_{2}$$
(4.1)



Figure 4.1: Schematic diagram of a 2D circular island of radius r with tangential force applied on its boundary.

where,

$$egin{aligned} m{f}_1 &= (f\cos heta_1,f\sin heta_1) \ m{f}_2 &= (f\cos heta_2,f\sin heta_2) \end{aligned}$$

and θ_i is the angle between f_i and the x axis.

Using the polar coordinate system, we have

$$|\boldsymbol{r_1} - \boldsymbol{r_2}| = 2r \left| \sin \frac{\theta_2 - \theta_1}{2} \right| \tag{4.2}$$

$$f_1 \cdot f_2 = f^2 \cos(\theta_2 - \theta_1) = f^2 (1 - 2\sin^2 \frac{\theta_2 - \theta_1}{2})$$
(4.3)

$$f_1 \cdot (r_1 - r_2) = -2fr \sin^2 \frac{\theta_2 - \theta_1}{2}, f_2 \cdot (r_1 - r_2) = 2fr \sin^2 \frac{\theta_2 - \theta_1}{2} \quad (4.4)$$

$$ds_1 = rd\theta_1, ds_2 = rd\theta_2 \tag{4.5}$$

Finally, we get the equations for the strain energy $E_{strain}^{1}(r)$ of a 2D island, which are

$$E_{strain}^{1}(r) = -\frac{(1+\nu)f^{2}}{4\pi E_{film}} \int_{0}^{2\pi} \int_{\theta_{0}}^{2\pi-\theta_{0}} \left[(1-\nu) \left(\frac{1}{\sin\frac{\theta_{2}-\theta_{1}}{2}} - 2\sin\frac{\theta_{2}-\theta_{1}}{2} \right) -\nu\sin\frac{\theta_{2}-\theta_{1}}{2} \right] d\theta_{1}d\theta_{2}$$

$$= -\frac{(1-\nu^{2})f^{2}}{\pi E_{film}} (2\pi r) \ln\frac{r}{a_{r}}$$

$$= -2\pi\alpha r \ln\frac{r}{a_{r}}$$
(4.6)

The variable θ_0 in Eq. (4.6) is an angular cutoff, and is given by

$$a_r = \frac{1}{4} e^{g(\nu)} a_e \tag{4.7}$$

where

$$g(\nu) = \frac{2-\nu}{1-\nu}$$
 (4.8)

$$\theta_0 = \frac{a_e}{r} \tag{4.9}$$

Here, a_e is a cutoff in real space of the order of lattice constant a_s . It is necessary for us to add the cutoff to our formula, in order to regularize a singular term. This is because the continuum elastic theory is not applicable to our lattice model at length sales comparable to a_s . In Eq. (4.6), α is defined by

$$\alpha = \frac{(1 - \nu^2)f^2}{\pi E_{film}}$$
(4.10)

4.2 3D n-layer cylindrical island

For a 3D island in cylindrical shape, the separation between two adjacent steps of the island is zero. As shown in Fig. 4.2, there is a general 2-layer island



Figure 4.2: Schematic diagrams of a general 2-layer island (left) and a 2-layer cylindrical island (right).

and a 2-layer cylindrical island. We now generalize Eq. (4.6) to a 3D n-layer cylindrical island. From simple scaling theory based on continuum elasticity, the strain energy is increased by n^2 times when the length scale of a structure is increased by n times. Hence we obtain the following functional form for the elastic strain relaxation energy $E_{strain}^n(r)$ for a 3D n-layer cylindrical island:

$$E_{strain}^{n}(r) = -2\pi\alpha n^{2}r\ln\frac{r}{na_{r}}$$

$$\tag{4.11}$$

4.3 The strain energy cross term

For a 3D island which is not in cylindrical shape, there are interactions between two strain fields due to different layers, which can further relax the strain energy of the island. In this section, we will calculate this strain energy cross term. Figure 4.3 shows the circular tangential load of force per unit length f applied radially on the circular boundary with radius r_1 . The circular tangential load generate a displacement field. At $r = r_2$, this displacement field interacts with another circular tangential load.


Figure 4.3: Circular tangential load applied on the circular boundary with radius r_1 . The generated displacement field interacts with another circular tangential load with radius r_2 .

By using Eq. (3.34), we can get the strain cross term $E_{strain}^{cross}(r_1, r_2)$ as

$$E_{strain}^{cross}(r_1, r_2) = -\frac{1+\nu}{2\pi E_{film}} f^2 \oint \oint \left((1-\nu) \frac{r_1 \cdot r_2}{|r_1 - r_2|} + \nu \frac{r_1 \cdot (r_1 - r_2) r_2 \cdot (r_1 - r_2)}{|r_1 - r_2|^3} \right) ds_1 ds_2$$
(4.12)

where in the polar coordinate system, we have

$$\boldsymbol{r}_1 \cdot \boldsymbol{r}_2 = r_1 r_2 \cos(\theta_1 - \theta_2) \tag{4.13}$$

$$|\boldsymbol{r}_1 - \boldsymbol{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos(\theta_1 - \theta_2)}$$
 (4.14)

$$ds_1 = r_1 d\theta_1, ds_2 = r_2 d\theta_2 \tag{4.15}$$

Then, we get the expression for $E_{strain}^{cross}(r_1, r_2)$, which is

$$E_{strain}^{cross}(r_1, r_2) = -2\pi\alpha \left(A(r_1, r_2) - \frac{2\nu}{1 - \nu} B(r_1, r_2) \right)$$
(4.16)

where α is given in Eq. (4.6). The first term $A(r_1, r_2)$ is

$$A(r_1, r_2) = \frac{-(r_1 + r_2)^2 \boldsymbol{E}\left[\frac{4r_1r_2}{(r_1 + r_2)^2}\right] + (r_1^2 + r_2^2)\boldsymbol{K}\left[\frac{4r_1r_2}{(r_1 + r_2)^2}\right]}{r_1 + r_2} \quad (4.17)$$

Here, K(x) and E(x) are the complete elliptic integrals of the first kind and the second kind which are defined as

$$\boldsymbol{K}(x) = \int_0^{\frac{\pi}{2}} \frac{d\theta}{\sqrt{1 - x \sin^2 \theta}}$$
(4.18)

$$\boldsymbol{E}(x) = \int_0^{\frac{\pi}{2}} \sqrt{1 - x \sin^2 \theta} \, d\theta \tag{4.19}$$

The second term $B(r_1, r_2)$ in Eq. (4.16) is given by

$$B(r_1,r_2) = egin{cases} r_1r_2, & r_1=r_2, \ 0, & r_1
eq r_2 \end{cases}$$
 (4.20)

which is non-zero only if $r_1 = r_2$.

4.4 Strain energy of n-layer circular island

We consider n-layer island with axisymmetric geometry, as shown in Fig.4.4. The radius of the *i*th layer is denoted by r_i , $r_i \ge r_{i+1}$. So that r_1 is the radius of the bottom layer while r_n is radius of the top layer. If $r_1 = r_2 = \cdots = r_n$, a general n-layer circular island reduces to an n-layer cylindrical island discussed in section 4.2.

Here, considering the step interactions, the strain energy for the n-layer circular island $E_{strain}^n(r_1, \dots, r_n)$ can be expressed as

$$E_{strain}^{n}(r_{1},\cdots,r_{n}) = -\sum_{i=1}^{n} \left(2\pi r_{i}\alpha \ln \frac{r_{i}}{a_{r}} + \sum_{j=1, j\neq i}^{n} E_{strain}^{cross}(r_{i},r_{j}) \right)$$

$$(4.21)$$



Figure 4.4: Schematic graph for an n-layer circular island

where the strain cross term $E_{strain}^{cross}(r_i, r_j)$ is given by Eq. (4.16).

4.5 Total island energy

By adding a step energy term $2\pi r\sigma$ into Eq. (4.6), total energy $E^1(r)$ for circular 2D island is given by

$$E^{1}(r) = 2\pi r \left(\sigma - \alpha \ln \frac{r}{a_{r}}\right)$$
(4.22)

Similarly, the total energy change for the formation of an n-layer circular island $E^n(r_1, \dots, r_n)$ consists of the elastic term $E^n_{strain}(r_1, \dots, r_n)$ in Eq. (4.21) and the step energy term which contains the entropic repulsion $\sum_{i=1}^n 2\pi r_i \sigma_{step}$. Therefore

$$E^{n}(r_{1},\cdots,r_{n}) = \sum_{i=1}^{n} \left[2\pi r_{i} \left(\sigma_{step} - \alpha \ln \frac{r_{i}}{a_{r}} \right) - \sum_{j=1, j\neq i}^{n} E^{cross}_{strain}(r_{i},r_{j}) \right]$$

$$(4.23)$$

4.6 Chemical potential

For a 2D island at local equilibrium, the chemical potential $\mu(r)$ at a local region can be derived from (4.22):

$$\mu(r) = \frac{\partial E^1}{\partial N} \tag{4.24}$$

$$= v \left(\frac{\sigma_{step} - \alpha}{r} - \frac{\alpha}{r} \ln \frac{r}{a_r} \right)$$
(4.25)

here, $v = a_s^2$ is the surface area per atom of the island.

Similar, for an n-layer island, if it subjects to certain constraint, for example the radial separation of two adjacent layer Δr is fixed, the chemical potential of the island can be obtained. The calculation of the chemical potential is much more complicated. A special case for calculating the chemical potential for nlayer island is given in section 5.4.

Chapter 5

Surface free energies

In this chapter, we will first introduce basic equations for the population of 2D islands at equilibrium in section 5.1. Then, we will study three distinct surface states which occur in island growth in slow deposition conditions, including states with respectively only subcritical islands in section 5.2, a stable 2D island and multiple subcritical islands in section 5.3 and a stable n-layer island and multiple subcritical islands in section 5.4. Finally, the equations for calculating the island nucleation rate and nucleation time are given in section 5.5.

5.1 Population of 2D islands at equilibrium

The equilibrium probability P(N) that surface site is occupied by a 2D island consisting of N atoms at low island density follows from the Boltzmann's distribution. We get

$$P(N) = \frac{\exp\left(-\frac{E(N)-\mu N}{k_B T}\right)}{1+\sum_{N} \exp\left(-\frac{E(N)-\mu N}{k_B T}\right)}$$
(5.1)

where E(N) is total energy change in forming an island consisting of N atoms, and μ is the chemical potential of the system. For low island density situation that we are interested at

$$\sum_{N} \exp\left(-\frac{E(N) - \mu N}{k_B T}\right) \ll 1$$

Therefore,

$$P(N) \approx \exp\left(-\frac{E(N) - \mu N}{k_B T}\right)$$
 (5.2)

The total coverage of the film materials equals

$$\theta = \sum_{N} NP(N) \tag{5.3}$$

$$= \sum_{N} N \exp\left(-\frac{E(N) - \mu N}{k_B T}\right)$$
(5.4)

5.2 Surface with multiple subcritical islands

At the beginning of a deposition process, only adatoms and other subcritical island can be found in the system because it takes time to overcome the energy barrier to form stable islands. In this thesis, we use (5.2) and (5.4) to determine the relationship between system's chemical potential μ and its coverage θ when only subcritical islands exist.

Here is how we define the chemical potential. Consider a system including only a kink site surrounded by a big reservoir. We define μ in such a way that, when a kink site and the reservoir are in equilibrium, $\mu = 0$.

The energy change in adding an adatom from the reservoir to the surface of the substrate for the ball and spring model explained in section 2.3 is exactly

$$E_{ad} = 2\gamma_{NN} + 2\gamma_{NNN} - E_s^0 \tag{5.5}$$

where E_s^0 is given by Eq. (3.22). For a subcritical island consisting of N atoms,

we use an effective radius r(N) defined by

$$r(N) = \sqrt{\frac{Na_s^2}{\pi}} \tag{5.6}$$

Substituting the effective radius into Eq. (4.6), we can calculate the energy change for forming a 2D island $E_1(N)$ by

$$E_1(N) = E^1(r(N))$$

= $2\pi r(N) \left(\sigma - \alpha \ln \frac{r(N)}{a_r}\right)$ (5.7)



Figure 5.1: Free energy versus island size. n^* is the critical size for island nucleation.

Consider only subcritical islands and neglect the stable ones at this moment, we apply a cutoff for the upper limit n^* in the sum in Eq. (5.4). Here, as we see in Fig. 5.1, n^* is defined to be the critical size of a 2D island, and is given by solving

$$\left. \frac{d(E(N) - \mu N)}{dN} \right|_{N=n^*} = 0 \tag{5.8}$$

Here, n^* depends on the system's chemical potential μ . When μ is well below zero, n^* tends to infinity. For $\mu \ge 0$, n^* decreases as μ increases. In summary, given the chemical potential of the system, the critical size n^* can be obtained numerically from Eq. (5.8). Therefore we can get the relationship between the coverage θ and the chemical potential μ of the system by using Eq. (5.4), as follows

$$\theta_0 = \sum_{N=1}^{n^*} N \exp\left(-\frac{E(N) - \mu N}{k_B T}\right)$$
(5.9)

From thermodynamics theory, chemical potential equals

$$\mu = \frac{dF_0}{dN} = \frac{1}{L^2} \frac{dF_0(\theta)}{d\theta}$$
(5.10)

Then the free energy for system with only adatoms and subcritical islands on the surface is given by

$$F_0(\theta) = L^2 \int_0^\theta \mu(\theta') \, d\theta' \tag{5.11}$$

5.3 Surface with a stable 2D island and multiple subcritical islands

After sufficient time of deposition, a stable 2D island will be observed. If the deposition rate is low enough, the system can be assumed to be in equilibrium. Then the chemical potential μ of the system is determined by the size of the 2D island using Eq. (4.25) in section 4.6. With the calculated μ , we can determine the coverage θ due to the subcritical islands using (5.9). Finally, total coverage of the surface is obtained by summing up the coverage due to subcritical islands and that due to a stable 2D island.

$$\theta_1 = \theta_0 + N_1 / L^2 \tag{5.12}$$

where N_1 is the number of atoms in the 2D island. The free energy for the system with a single stable 2D island is similarly given by

$$F_1(\theta) = F_0(\theta - N_1/L^2) + E_1(N_1) - k_b T \ln L^2$$
(5.13)

5.4 Surface with a stable n-layer island and multiple subcritical islands

Similarly, the total coverage for a system with a single stable n-layer island and multiple subcritical islands θ_n is then given by

$$\theta_n = \theta_0 + N_n / L^2 \tag{5.14}$$

where N_n is the number of atoms of the n-layer island.

The free energy for system with a stable n-layer island and multiple subcritical islands F_n is given by

$$F_n(\theta) = F_0(\theta - N_n/L^2) + E_n(N_n) - k_b T \ln L^2$$
(5.15)



Figure 5.2: Schematic diagram of a general stacked 2-layer circular island. r_1 is the radius of the bottom layer; r_2 is the radius of the top layer. The constraint for two-layer island is $r_1 = r_2 + \Delta r_{12}$.

Here, assuming equilibrium, the chemical potential μ is determined from the size and the geometry of the stable n-layer island. Take 2-layer island as shown in Fig. 5.2 as an example, we calculate the chemical potential μ for this particular system. In Fig. 5.2, r_1 is the radius of the bottom layer while r_2 is the radius of the top layer. Assuming a constant difference Δr_{12} between r_1 and r_2 , i.e. $r_1 = r_2 + \Delta r_{12}$, the chemical potential μ is obtained by

$$\mu = \frac{\partial E_2(N)}{\partial N} \bigg|_{N=N_2}$$
(5.16)

Here, $E_2(N)$ can be derived using Eq. (4.23) and we obtain

$$E_2(N) = E^2(r_1, r_2)$$

= $2\pi r_1 \left(\sigma - \alpha \ln \frac{r_1}{a_r} \right) + 2\pi r_2 \left(\sigma - \alpha \ln \frac{r_2}{a_r} \right) + 2\pi (r_1 + r_2) \tilde{\sigma}$
 $- \left(E_{strain}^{cross}(r_1, r_2) + E_{strain}^{cross}(r_1, r_2) \right)$ (5.17)

where, r_1 and r_2 follow

$$\pi(r_1^2 + r_2^2) = Na_s^2 \tag{5.18}$$

$$r_1 = r_2 + \Delta r_{12} \tag{5.19}$$

Furthermore, $\tilde{\sigma}$ is the correction of step energy due to entropic repulsion considered step repulsion in Eq. (3.11) in section 3.2.

In the same way, we can obtain the chemical potential μ for a n-layer circular island if certain appropriate constraint is given.

5.5 Island nucleation rate and nucleation time

The island nucleation rate per atomic site rate J_s is the rate at which a new stable island or a new top layer nucleates in the system. We calculate J_s by [20]

$$J_s = z f^* c^* \tag{5.20}$$

The first term z in Eq. (5.20) is called the Zeldovich factor and is given by

$$z = \left[-\frac{1}{2\pi k_B T} \frac{d^2 W(N)}{dn^2} \Big|_{N=N^*} \right]^{\frac{1}{2}}$$
(5.21)

where W(N) is the free energy for a system with an island consisting of N atoms. The second term f^* in Eq. (5.20) is called the adatom attachment rate and is calculated by

$$f^* = \frac{1}{4\Delta t} \frac{2\pi r}{a_s} \rho_a \tag{5.22}$$

in which

$$\Delta t = \frac{a_s^2}{2D} \tag{5.23}$$

$$D = D_0 e^{-\frac{E_a}{k_B T}} \tag{5.24}$$

where Δt is the adatom hopping time, D is the adatom diffusion coefficient, and ρ_a is the adatom density. The values for E_a and D_0 used are given by

$$E_a = 0.67 \text{eV} \tag{5.25}$$

$$D_0 = 3.83 \times 10^{13} \text{\AA}^2 \text{ s}^{-1} \tag{5.26}$$

The third term c^* in Eq. (5.20) refers to the critical nucleus concentration and is given by

$$c^* = c_0 e^{-\frac{W^*}{k_B T}} \tag{5.27}$$

where W^* is the work of formation. For our case, c^* is given by

$$c^* = \frac{1}{Z} e^{-\frac{F^*}{k_B T}}$$
(5.28)

 F^* is the total free energy of the system, and Z is given by

$$Z = \sum_{n=0}^{n^*} e^{-\frac{E_n - \mu n}{k_B T}}$$
(5.29)

The nucleation time t_c equals

$$t_c = \frac{1}{J_s \cdot N_c} \tag{5.30}$$

where N_c here is the number of nucleation sites where an island can be formed.

Chapter 6

Applications to Kinetic Monte Carlo simulation results

6.1 Simulation results

In this section, we discuss the simulation results calculated from 11 independent runs for the deposition of a heteroepitaxial films at T = 600K, with low deposition rates 1ML s⁻¹, 3ML s⁻¹ and 10ML s⁻¹ [13]. The nominal misfit for the system is 8%.

6.1.1 Surface morphology

Under the low rate deposition condition, we can observe the layer-by-layer island growth mechanism from the surface morphological evolution results of the simulation. Figure 6.1 is an example, which shows the surface morphology from a typical run for deposition rate = $3ML s^{-1}$. Initially, there are only adatoms and subcritical 2D islands on the surface without any wetting layer as shown in Fig. 6.1(a). Next, a small 2D stable island emerges as shown in Fig. 6.1(b). We can see more than one 2D island on the surface as more atoms are deposited on

the surface as shown in Fig. 6.1(c). Then, as the surface coverage θ increases, 2D to 3D island transition occurs. A new layer of atoms nucleates on top of one of the 2D islands, leading to the formation of a 2-layer island. Other 2D islands are dissolved as the 2-layer island grows laterally [Fig. 6.1(d)]. When the 2-layer island is large enough, a new top layer forms again and the 2-layer island becomes a 3-layer island [Fig. 6.1(e)]. Repeatedly, the island formation follows a layer-by-layer growth mode, from 3-layer to 4-layer [Fig. 6.1(f)], then to 5-layer [Fig. 6.1(g)]. Moreover, steps separation decrease as island grows vertically. We can see that the steps in the 5-layer island in Fig. 6.1(g) are closer than those in the 2-layer island in Fig. 6.1(d).



Figure 6.1: Surface from simulation of deposition at T = 600K, for deposition rate = 3ML s⁻¹ at deposit time t = 0.0052(a), 0.0221(b), 0.07902(c), 0.11(d), 0.126(e), 0.202(f), 0.284s(g). The surface coverage θ is 0.0156(a), 0.0663(b), 0.23706(c) 0.33(d), 0.378(e), 0.606(f) and 0.852(g).

6.1.2 Strain energy per atom

In the simulation, the strain energy of the whole system is calculated repeatedly during the whole deposition processes. The results for strain energy per film atom E_s are shown in Fig. 6.2. The figure highlights two processes: top layer nucleation and island lateral growth. Strain energy per atom decreases when a new layer nucleates on top, and increases gradually as the dominant island grows laterally larger without forming a new layer. These can be explained by the continuum elasticity theory.



Figure 6.2: Strain energy per atom E_s versus film coverage θ . The figure is obtained from 11 independent simulations of deposition at T = 600K, with deposition rates 1ML s⁻¹, 3ML s⁻¹ and 10ML s⁻¹.

6.1.3 Chemical potential measurement

Based on the ball and spring model, we now try to calculate the adatom occupation probability r. The probability for a system consisting of N film atoms to have one more adatom on its surface P_{N+1} is given by

$$P_{N+1} = P_N e^{-\frac{E_{ad}-\mu}{k_B T}} \tag{6.1}$$

where the adatom energy E_{ad} can be calculated using Eq. (5.5), and P_N is the probability of the defined system to occur. Hence, r is given by

$$r = \frac{P_{N+1}}{P_N} \tag{6.2}$$

$$= e^{-\frac{2\gamma_N - 2\gamma_{NN} + E_s^0 + \mu}{k_B T}}$$
(6.3)

The adatom density is calculated by

$$P_{ad} = \frac{r}{1+r} \tag{6.4}$$

Hence, the chemical potential can be obtained by counting the adatom density on the surface.

Figure 6.3 is the result of chemical potential measurement. From this figure, we can see an initial rise of the chemical potential, because the number of adatoms is increasing before 2D stable islands occur. Next, island lateral growth results in a small increase of the chemical potential. Then, when a layer of atoms nucleate on top of the island, there will be a decrease in the chemical potential of the system.



Figure 6.3: Chemical potential μ versus θ from 11 independent simulations of deposition at T = 600K, with deposition rates 1ML s⁻¹, 3ML s⁻¹ and 10ML s⁻¹.

6.2 Regularization for the strain cross term

We have derived the equations for the strain energy cross term in section 4.3.



Figure 6.4: The strain cross term $E_{strain}^{cross}(r_1, r_2)$ versus r_1 with $(r_2 = 10\text{\AA})$ when assuming a line force per unit step length $f = 0.1 \text{eV/\AA}^2$. There is a singularity at $r_1 = r_2$

Figure 6.4 shows the strain cross term $E_{strain}^{cross}(r_1, r_2)$ versus r_1 with a fixed r_2 ($r_2 = 10$ Å), when assuming the radial tangential force per unit length $f = 0.1 \text{eV}/\text{Å}^2$, calculated using Eq. (4.16). Here, the elastic constants we use are $E_{film}=40 \times 10^9 \text{Nm}^{-2}$ and $\nu=0.25$, which are calculated by Eq. (3.19) and Eq. (3.20). The figure shows that $E_{strain}^{cross}(r_1, r_2) \rightarrow 0$, when $r_1 \rightarrow 0$ or ∞ . There is a singularity in the radial displacement at $r_1 = r_2$, i. e. $\lim_{r_1 \rightarrow r_2} E_{strain}^{cross}(r_1, r_2) = \infty$, due to $\mathbf{K}(x)$ in Eq. (4.17) at x = 1.

In order to suppress the singularity, we add an angular cutoff θ_c into Eq. (4.18)



Figure 6.5: The regularized strain cross term $E_{strain}^{cross}(r_1, r_2)$ versus r_1 with $r_2 = 10$ Å. The value for $E_{strain}^{cross}(r_1, r_2)$ with cutoff θ_c given in Eq. (6.7) equals $E_{strain}^1(r_1)$ (Dashed curve) at $r_1 = r_2 = 10$ Å.

and Eq. (4.19). The modified expressions for $K^{c}(x)$ and $E^{c}(x)$ are given by

$$\boldsymbol{K}^{c}(x) = \int_{0}^{\frac{\pi}{2}-\theta_{c}} \frac{d\theta}{\sqrt{1-x\sin^{2}\theta}}$$
(6.5)

$$\boldsymbol{E}^{c}(x) = \int_{0}^{\frac{n}{2}-\theta_{c}} \sqrt{1-x\sin^{2}\theta} \, d\theta \qquad (6.6)$$

If the angular cutoff θ_c vanishes, $\mathbf{K}(x)$ and $\mathbf{E}(x)$ reduces to the complete elliptic integrals of the first and the second kind respectively. In our calculation, a finite θ_c of the order $\frac{a_s}{r_i}$ or $\frac{a_s}{r_j}$ is needed to suppress the singularity in $\mathbf{K}(x)$ at x = 1. Also, $B(r_1, r_2)$ is assumed to be zero for both $r_1 = r_2$ and $r_1 \neq r_2$ to avoid the discontinuity which is not physical. Specifically, we put

$$\theta_c = \frac{2a_r}{e^2 \max\{r_i, r_j\}} \tag{6.7}$$

so that elastic energy given by Eq. (4.21) for an *n*-layer island reduces properly to that for a single layer island in Eq. (4.6) for n = 1. Furthermore, this choice

preserves the symmetry $A(r_i, r_j) = A(r_j, r_i)$ inherented from an analogous symmetry in the Green's function G. With the same values for r_2 and the line force per unit step length f in Fig. 6.4, the regularized strain $E_{strain}^{cross}(r_1, r_2)$ versus r_1 is shown in Fig. 6.5, where we put the spatial cutoff $a_r = a_s$.

6.3 Island strain energy

6.3.1 n-layer cylindrical islands

Although the formula for strain energy is given in the previous chapter, the cutoff a_r is needed to be evaluated numerically by comparing with our KMC simulations. We first consider a system with only one cylindrical n-layer island



on the substrate and we neglect adatoms and other subcritical islands. Therefore

the number of the atoms in the island is

$$N = L^2 \theta = \frac{\pi r^2 n}{a_s^2} \tag{6.8}$$

where $r = a_s \sqrt{\frac{L^2 heta}{n \pi}}$ is the radius of the cylindrical n-layer island.

We rewrite Eq. (4.11) as

$$-\frac{E^n(r)}{rn^2} = 2\pi\alpha \ln\frac{r}{na_r}$$
(6.9)

$$= c_1 \ln \frac{r}{n} - c_2 \tag{6.10}$$

where $c_1 = 2\pi\alpha$ and $c_2 = 2\pi\alpha \ln a_r$. To check Eq. (6.10) against our simulation,

number of layer n	ε	na_r
2	0.111268	$1.48029a_s$
3	0.100547	$1.83178a_s$
4	0.0953564	$2.14549a_s$
5	0.0930275	$2.52215a_s$

Table 6.1: Fitting parameters by applying formula for cylindrical n-layer island.

we plot $\frac{E^n(r)}{rn^2}$ against $\frac{r}{n}$ and the result is shown in Fig. 6.6. Most data points for $n \ge 2$ lie close to the same straight line, implying that Eq. (6.10) which is for cylindrical island describes the system quite well. This is not true for points from the 2D islands (n = 2). The discrepancy is due to the fact that the system has more than one 2D island on the substrate, and hence our assumptions do not stand. Fitting the data to Eq. (6.10) independently for n = 2, 3, 4, and 5, we obtain ε and a_r , listed in Table 6.1. The fitted curves are shown in Fig. 6.7 and Fig. 6.8. Effective values for the misfit are introduced here. We believe that the difference between the effective misfit and the nominal misfit is mostly due to inaccuracy in the small-slop approximation used. The fitted effective misfits decrease while number of layer of the island increases. The cutoffs differ too.



Figure 6.7: Fitting result for (a)n=2; (b)n=3; (c)n=4; (d)n=5;



Figure 6.8: Strain energy per atom fitting result by applying formula for cylindrical n-layer island

6.3.2 n-layer truncated cone islands with $\Delta r = a_s$

We similarly take the same assumption that the dominant island holds all the film atoms. But rather than assuming cylindrical islands, we now suppose that the separation of the edges of the adjacent layers is a_s , as it is about $1 \sim 2a_s$ for the islands we observed in the simulations. Therefore, the radii of the adjacent layers differs by $\Delta r = a_s$. Then, given a coverage θ , the shape of an n-layer island can be determined. We have repeated the fitting by applying Eq. (4.23) for general circular island. Table 6.2 shows the results.

number of layer n	ε	a_r/n
2	0.113065	$1.35732 \ a_s$
3	0.102726	$1.56854 a_s$
4	0.097557	$1.71215 \ a_s$
5	0.095246	$1.93232 a_s$

Table 6.2: Fitted parameters for n-layer islands following $\Delta r = a_s$.

Compared with Table 6.1, the effective values for the misfit are similar. Increasing the number of island layers results in a decrease in the effective misfit. The trend for the cutoff change as the number of layer n increases is the same. a_r is more or less proportional to n. But the values are somewhat different, because the cutoff is more sensitive to the change of island shapes.

6.4 Deposition



Figure 6.9: Plot of effective misfit against number of layer n of an island. The effective curve is $\varepsilon(n) = 0.0802764 + 0.0616312/n$, which extrapolates to $\varepsilon(1) = 0.141908$



Figure 6.10: Plot of effective cutoff against number of layer n of an island. The effective curve is $a_r(n) = 0.342478 + 0.796072/n$, which extrapolates to $a_r(1) = 1.13855a_s$

In the previous two sections, we neglect subcritical islands. In this section, we will consider the impact of the subcritical islands under deposition conditions, by using the equations presented in Chapter 5. Here we use the layer-dependent

effective values for misfit and cutoff shown in Table 6.1. For $n \ge 2$, the effective misfit and cutoff in section 6.3.1 can be well approximated by the phenomeno-logical formulas

$$\varepsilon(n) = 0.0802764 + 0.0616312/n \tag{6.11}$$

$$a_r(n) = 0.342478 + 0.796072/n \tag{6.12}$$

as shown in Fig. 6.9 and Fig. 6.10. Expolating to n = 1, we have $\varepsilon(1) = 0.141908$ and $a_r(1) = 1.12305a_s$.

When we use Eq. (5.9) to determine the relationship between the coverage θ_0 and the chemical potential μ for a system with only subcritical islands, we consider only adatoms. We have check that in our KMC simulation, subcritical islands are dominated by adatoms, so we believe that considering only adatoms is a good assumption in our case. Moreover, when substituting the effective values for misfit and cutoff to Eq. (5.8), the critical size for 2D island n^* is only several atoms, implying that the size of subcritical islands is small. However, the energy change for forming a subcritical 2D island consisting of N atoms $E_1(N)$ (N > 1) can not be accurately obtained for small islands, when applying Eq. (5.7) which assumes the continuum approximation. Also, for simplicity, we assume that there is at most one stable island with multiple adatoms in the system, as discussed in section 5.3 and section 5.4.

Figure 6.11 shows the chemical potential versus coverage for a system with only adatoms (solid curve) and a system with a single stable 2D island and multiple adatoms (dashed curve) which are calculated numerically using Eq. (5.2), (5.9), and (5.12). For a system with adatoms only, there is an initial rise in the chemical potential at the beginning of the deposition, because the number of adatoms increases as more atoms deposit onto the substrate. From the solid curve, we can see that no stable 2D island can occur until $\theta = 0.021$. There is a minimum chemical potential $\mu \approx -0.017812$ eV which occurs at coverage $\theta = 0.040988$. The size of the dominating 2D island related to the minimum is



Figure 6.11: Chemical potential versus coverage for system with only adatoms (dashed curve) and system with a single stable 2D island and multiple adatoms (solid curve).

about 29 atoms. The chemical potential tends to 0 when coverage is very large, i.e. $\lim_{\theta \to \infty} \mu \to 0$.



Figure 6.12: Free energy F_1 versus island size N_1 at $\theta = 0.03$. Point A is a minimum of the free energy and point B is the free energy for a system with only adatoms

Figure 6.12 shows the free energy for a system with a single 2D island and adatoms versus the 2D island size calculated using Eq. (5.13). From this figure, we can see that the free energy has a minimum at $N_1 = 19$ (point A). The 2D island and the adatoms have the same chemical potential at point A which represents a stable equilibrium state. Point B is the energy for a system with only adatoms. The free energy difference between A and B corresponds to the energy barrier for the formation of a stable 2D island at a fixed coverage. There is no energy barrier for 2D island formation in Fig. 6.12.



Figure 6.13: Free energy versus coverage θ for system with only adatoms (dashed curve) and system with a single stable 2D island and adatoms (solid curve) at equilibrium.

Figure 6.13 shows the free energy versus coverage for a system with only adatoms (dashed curve) and a system with a single island and adatoms (solid curve) at equilibrium. From the dashed curve, we can see that there is a minimum at $\theta_0 = 0.018$, which corresponds to chemical potential for adatoms $\mu = 0$. From the solid curve, we can see that stable 2D island cannot occur at the early stage of deposition until a critical coverage ($\theta = 0.021$). However, once a 2D island forms, the free energy for the system decreases suddenly.

Similarly, we can find the stable equilibrium state for a system with a single stable n-layer island and adatoms. Similar to Eq. (5.14) and (5.12), the total coverage for a system with subcritical islands and a single stable n-layer island θ_n is then given by

$$\theta_n = \theta_0 + N_n / L^2 \tag{6.13}$$

The free energy for a system with a stable n-layer island and multiple subcritical islands is given by

$$F_n(\theta) = F_0(\theta - N_n/L^2) + E_n(N_n) - k_b T \ln L^2$$
(6.14)

Actually, we need not find the minimum to obtain the stable equilibrium state every time when the film coverage is large. This is because the stable island dominates the system when the coverage is very large. The chemical potential for a stable island is always negative. When a stable island and adatoms are in equilibrium, $\mu < 0$. According to the relationship between chemical potential and the film coverage due to adaoms calculated using Eq. (5.9), the film coverage due to adaoms follows $\theta_0 < 0.018$. Therefore, it is still a good assumption that all of the atoms are incorporated to the island, as we assume in section 6.3.1 and 6.3.2. Then the approximate equations are given by

$$\theta_n = \theta_0 + N_n / L^2 \approx N_n / L^2 \tag{6.15}$$

and

$$F_n(\theta) = F_0(\theta_0) + E_n(N_n) - k_b T \ln L^2$$
(6.16)

where θ_0 is determined by the chemical potential of the island by using Eq. (5.9).

6.5 Equilibrium shape for n-layer truncated cone island

We adopt the assumption that when a 3D island is at local equilibrium, the difference between the radii of every adjacent layer Δr is the same, i. e., the island keeps the shape of an n-layer truncated cone. Considering step repulsion in section 3.2, the free energy for an n-layer island $E^n(r_1, \dots, r_n)$ in Eq. (4.23) have a minimum with respect to the step distance Δr , when the volume of the island is fixed. Figure 6.14 shows the free energy versus $\frac{\Delta r}{a_s}$, when substituting ε =0.1, $a_r = a_s$ into Eq. (4.23) at $\theta = 0.2$. The minimum which occurs at Δr =1.65975 a_s represents the equilibrium shape for the 3D island by using the set of effective values for misfit and cutoff.



Figure 6.14: Free energy versus step distance for 2-layer island. Here, we use, $\varepsilon = 0.1$, $a_r = a_s$. The minimum of the free energy occurs at $\Delta r = 1.65975 a_s$

In our case, the effective values for misfit and cutoff are unknown. Hence in order to get the equilibrium shape for a 3D island, we introduce a self consistent approach in this section. On the one hand, if step separation Δr is given, we can use the general formula in Eq. (4.23) to fit the simulation result of the strain energy per atom as shown in Fig. 6.2 in section 6.1.2. On the other hand, once we get the effective values for misfit and cutoff, Δr corresponding to the equilibrium shape is determined. After several iterations, we can get the equilibrium shape for a 3D island and the fitted effective values for misfit and cutoff. The results are listed in Table 6.3. From the table, Δr specifies the equilibrium shape for n-layer

number of layer	ε	a_r	Δr
1	0.148052	$0.97659 \ a_s$	_
2	0.112507	$1.07384 a_s$	$1.70588 \ a_s$
3	0.102173	$1.25807 a_s$	$1.38807 \ a_s$
4	0.097125	$1.43969 a_s$	$1.22908 \ a_s$
5	0.094978	$1.73001 a_s$	$1.12894 a_s$

Table 6.3: Fitting parameters by applying general formula.

circular islands. The separation Δr between the steps at adjacent layer decreases when the number of layers of the island increases accompanying deposition. It means that the surface inclination of the truncated cone increases as it grows vertically, which match the simulation observations introduced in section 6.1.1.



Figure 6.15: Strain energy per atom fitting result using the self consistent approach.

6.6 Upper layer nucleation

6.6.1 Surface free energy

Once we get Δr , the effective values of misfit and cutoff, we can substitute they in to Eq. (5.11) and Eq. (5.15) to calculate the free energies of the deposition system in different stages. Figure 6.16 shows the free energy F_n versus coverage θ for an n-layer island with the equilibrium shape. In Fig. 6.16, the free energy F_n for n = 2 at $\theta \simeq 0.45$ is the lowest compared to the free energy F_n for n > 2. As the coverage θ increases, both F_2 and F_3 decreases. But F_3 decreases even faster. Then, there is an intersection between F_2 and F_3 at $\theta \simeq 0.58$. This indicates that as the coverage becomes larger, an island with 3 layers is more stable than an island with 2 layers. Similar intersections happens for F_3 and F_4 at $\theta \simeq 0.73$, and for F_4 and F_5 at $\theta \simeq 1.13$ (See the first column in Table 6.4). It is clear that if the deposition is slower than the upper layer nucleation dynamics, the island will follow a layer-by-layer growth mode.



Figure 6.16: Free energy for n-layer island taking into account step repulsion.



Figure 6.17: Chemical potential versus θ taking into account step repulsion.

Figure 6.17 is the chemical potential for an n-layer island for section 6.5 as θ increases compared with the simulation result. The solid curve in Fig. 6.17 is the calculated chemical potential, and the point is the simulation result. The trend for the chemical potential is that, at small θ , there is an initial rise of the chemical potential. The lateral growth of island results in a small increase in the chemical potential while the top layer nucleation result. However, the values do not match very well. A possible reason for the vertical shift of the values can be approximations taken in calculating surface step free energies and so on.

6.6.2 Energy barrier and nucleation rate

To check our model, we also calculate the nucleation rate and time for the upper layer nucleation process.



Figure 6.18: Energy barrier for 2 to 3 layer island transition for $\theta = 0.575572$.

In order to obtain the energy barrier for the transition from the initial state of an n-layer island to the final state of an (n+1)-layer island, we introduce a



Figure 6.19: Radius for each layer for 2 to 3 transition for $\theta = 0.575572$.

reactive parameter ϕ in the way that $\phi = 0$ represents the initial state, and $\phi = 1$ refers to the final state. Parameters including the misfit ε , the cutoff a_r and the number of atoms of the top layer r_i change linearly between $\phi = 0$ and $\phi = 1$. We calculate the free energy $F(\phi)$ versus ϕ . Figure 6.18 shows the free energy versus ϕ for a 2-layer to 3-layer island transition at $\theta = 0.575572$ which is the transition point for F_2 and F_3 in Fig. 6.16 using the parameters listed in Table 6.3. Figure 6.19 shows the radius change for each layer correspond to ϕ . We get a transition barrier $E_b = 0.505517$ eV at $\phi = 0.150074$.

number of layer	θ	E_b (eV)	J_{s} (s ⁻¹)	$t_c(s)$
2 to 3	0.575572	0.505517	2.2745	0.003683
3 to 4	0.733908	0.551847	1.1392	0.010908
4 to 5	1.125860	0.645815	0.1870	0.067884

Table 6.4: Nucleation barrier, rate and time for upper layer nucleation.

Using using Eq. (5.20) and Eq. (5.30), we obtain the upper layer nucleation rate $J_s = 2.2745s^{-1}$ and the transition time $t_c = 0.003683s$. It means that it is easy for the island to overcome the energy barrier and transit from a 2-layer island to a 3-layer island at $\theta = 0.575572$.

The calculated nucleation rate and time for n to (n+1) layer transition at the free energy crossing points found in Fig. 6.16 are listed in Table 6.4. From the table, we can see that the nucleation time for 3 to 4 layer transition and 4 to 5 layer transition at the crossing points is in the order of 0.01s. We can see that the upper layer nucleation dynamics is fast relative to the deposition. Thus our theory verifies that the formation of island follows a layer-by-layer growth mode.
Chapter 7

Conclusions

In conclusion, we have introduced a layer-by-layer growth model to study the morphological evolution of strained heteroepitaxy under slow deposition condition. Using continuum elastic theory, we have investigated the strain energy for 2D circular islands, cylindrical n-layer circular islands, and stacked nlayer circular islands. Using the result of a Kinetic Monte Carlo simulation, we introduce correction to the small-slope approximation by using effective values of misfits and elastic cutoff. The step free energy with an entropic step repulsion term for a ball and spring model in a simple cubic lattice is calculated.

We have obtained the equilibrium shape of a 3D island by applying a self consistent approach. The separation between two adjacent steps Δr of an n-layer island decreases when the number of layers of the island increases accompanying deposition. The free energies for a system with a single n-layer island and subcritical islands have been presented and analyzed. Energy barriers for island transition and new layer nucleation time have been estimated. These results verify that island nucleation follows a layer-by-layer growth mode. A new layer of atoms can nucleate on top of an n-layer island only after the island grows laterally larger. There is an initial rise for the chemical potential of the system before forming stable 2D island. The process of island growing laterally results in a small increase in the chemical potential of the system, while a new layer of atoms nucleated on top of the island causes a sharp decrease of the system's chemical potential.

We expect that the similar analysis using this model can be applied to related heteroepitaxial systems as well. For example, it can be applied to systems with different values of misfit, lattice constant and elastic constant and so on. It can also be applied to structures with different geometries, such as pit, which was also observed in the KMC simulations under certain conditions.

This thesis focuses mainly on static thermodynamic analyses and the stability of the system. For future study, more efforts are needed to study the dynamics of island growth. Moreover, our study is limited to systems with only one stable island on the surface of the substrate. For future study, it is of interest to study systems with more than one stable island, by considering island interactions which are related to the shapes of the islands and their locations.

For the KMC simulations, the following problems are suggested. First, facets are commonly obtained in the growth of strained islands. In the experimental studies of Ge/Si and $\text{Ge}_x\text{Si}_{1-x}/\text{Si}$ heteroepitaxial systems, hut islands with (105) facets were obtained. The rebonded step reconstruction in faceted surface can further reduce the surface energy of an island. The question is, how the inclined surface consists of steps as described in this thesis becomes a faceted one? Second, to obtain an array of regularly-located self-assembled islands in the experiments, the use of patterned substrate were reported. How does the substrate affect the surface evolution of the heteroepitaxial systems? We can attempt to answer the above questions using our KMC simulation model in the coming future.

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