ANALYSIS OF THE SPIRAL GROWTH MECHANISM OF MOCVD SEMICONDUCTORS

by

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ABSTRACT

Although as a growth technique, metalorganic chemical vapor deposition (MOCVD) has been commercialized and used for both research and industry for a long time, very little is known from a crystal growth point of view. Compared with the growth from solution or melt, MOCVD growth, which involves a lot of sub-processes, is much more complicated. Growth parameters like the critical radius, surface diffusion length, supersaturation, specific surface free energy are very important for the description of crystal growth techniques in general.

In the growth from solution for example, the magnitude of concentration of the solute, which is related to a lot of growth parameters, can be easily measured. The same thing cannot be done for MOCVD. Also, there are few in situ techniques to monitor the movement or configuration of atoms.

The morphology information from spiral growth offers a way to solve this problem. Spiral growth theory provides the means to relate spiral morphologies (dislocation density, inter-step spacing, step height, hollow core radius, etc.) to growth parameters. Atomic force
microscopy (AFM) is a very useful technique for obtaining key morphology information needed by the theory. For the first time, MOCVD growth parameters are estimated by the measurements on spirals and the application of spiral growth theory for the two technologically important III-V semiconductors, InAs and GaSb.
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Chapter 1. Introduction

This thesis consists of three major parts. The theoretical part introduces the original and refined BCF theory, the theory of hollow core, and the theory of metalorganic chemical vapor deposition (MOCVD). The experimental part introduces the MOCVD setup, the atomic force microscopy (AFM) instrumentation, and the sample preparation procedure. The data analysis part introduces the extraction of growth parameters and discusses the physical meaning of these parameters.

1.1 Spiral growth theory

There are two major growth mechanisms concerning the microscopic picture of crystal growth. The first one is the nucleation growth mechanism. Just like the formation and growth of a water droplet in a supersaturated ambient, a crystal island of monolayer step height forms on the surface and will grow if its size exceeds the critical one. The concept of critical size or critical radius will be discussed in detail
later. Fig. 1 shows the nucleation mechanism which is usually observed in crystal growth by MBE.

\[ \text{Figure 1: The nucleation growth mechanism [44]} \]

Mobile adsorbed atoms keep incorporating into the edge of the islands until the top layer growth finishes. New islands will form again and the growth continues. The nucleation mechanism was well developed theoretically [3] [4] and verified experimentally [5]. The introduction of nucleation theory is out of the scope of this thesis and we only show some results here. The saturation ratio \( \alpha \) in the vapor phase is defined as the ratio of the actual pressure to the pressure required to establish thermal equilibrium with the solid phase. The supersaturation \( \sigma \) is defined as
co. = α−1. Nucleation theory in the case of monolayer growth leads to a critical supersaturation below which the growth cannot take place. [6]. This is related to the concept of the critical nucleus which we discuss in detail later. However, real crystals can grow at a supersaturation much lower than the critical supersaturation predicted by the nucleation theory. This implies that there must be other mechanisms for crystal growth [6]. In 1951, Burton, Cabrera and Frank (BCF) published their famous paper ‘THE GROWTH OF CRYSTALS AND THE EQUILIBRIUM STRUCTURE OF THEIR SURFACES’ [6]. According to BCF theory, crystals can grow due to screw dislocations which result in the presence of a permanent source of step edges. Fig. 2 shows what a screw dislocation looks like and what is the Burgers vector in the case of a screw dislocation. The vertical dash line in Fig. 2 is called dislocation line. The screw dislocation may be thought as produced by cutting the crystal partway through with a knife whose edge is parallel to the dislocation line, shearing it parallel to the dislocation line by length b and rejoining the displaced part to the part of crystal below in a way that preserves the basic crystalline order everywhere except near the dislocation line itself. Clearly, b must be equal to one or several lattice constant in order to
restore the basic order of the perfect crystal. The Burgers vector \( \mathbf{b} \) in the case of screw dislocation is defined as a vector pointing upwards, being parallel to the dislocation line and having a magnitude of \( \mathbf{b} \).

Figure 2. A screw dislocation and the definition of Burgers vector[50].

Unlike nucleation, in which the source of growth (islands) will terminate with the top layer of growth completed, spiral growth has a never ending source of nucleation sites at step edges. This idea is illustrated in Fig. 3.
Using thermodynamics and kinetic theory, BCF theory is able to quantitatively relate the morphology of a spiral (radius of curvature, inter-step spacing, etc.) to its growth parameters such as temperature, supersaturation, edge energy, surface diffusion length, etc. The main aspects of BCF theory have been verified experimentally, although many refinements were made later. For a good review paper, readers are referred to [7]. One of the refinements used in this paper is the theory of "back
force" effect. Also, in section 2.2 of this thesis, the theory of hollow core formation at the dislocation center will be introduced.

1.2 MOCVD

Metalorganic chemical vapor deposition (MOCVD) is a very efficient method to grow semiconductor compounds and heterostructures. In a typical MOCVD growth session, organometallic compounds such as trimethylindium(TMI) and tertiarybutylarsine(TBA) are transferred into the chamber by a carrier gas like nitrogen or hydrogen. These organometallic compounds are decomposed near or on a heated substrate and then the inorganic elements form a semiconductor compound on the substrate via one or more chemical reactions. In contrast with the situation in molecular beam epitaxy (MBE), in which group III and group V molecular beams impinge on a heated surface in ultra high vacuum, in MOCVD, source gases are introduced simultaneously with a carrier gas such as hydrogen at pressures from 0.1 to 1.0 atmosphere. A detailed microscopic theory of MOCVD is hard to establish because it involves a lot of poorly characterized processes and one has to consider hydrodynamic factors too. In addition there are few in situ techniques
available for monitoring the growth. There has been very little work done so far to discuss MOCVD within the framework of crystal growth theories. Nevertheless, the modern compound semiconductor device industry uses more and more wafers grown by MOCVD because of its efficiency and high quality.

1.3 Atomic Force Microscopy

An atomic force microscope (AFM) is an opto-mechanical instrument, which detects atomic-level forces (~nN). Most AFMs have vertical resolution below 0.1 nm, whereas the lateral resolution is around 10 nm. A lot of technologies (very sharp tip fabrication technology, cantilever technology, piezoelectric transducers, semiconductor lasers, small signal detection and processing technology, etc.) allow an AFM to "see" structures with atomic resolution in the vertical direction. Using an AFM image, we can easily measure the width of a terrace, the height of a step, the hillock or pit density on the surface and the radius of a hollow core, etc. all of which are very useful for both theory and device
applications. A detailed description of the working mechanism of AFM can be found in section 3.2 of this thesis.

1.4 Extraction of growth parameters

In the data analysis part of this thesis, we first review a new method for estimating the dislocation density of a semiconductor sample. Dislocation density is a very important parameter for device fabrication. This method, which was suggested by Dr. S. P. Watkins [25] estimates the dislocation density by counting the number of dislocation hillocks on large scale (at least 50 x 50 μm) AFM images. Next, we discuss the physical meaning of multi-branch and mono-atomic step height found in spirals. Then we present the result of growth parameter extraction for InAs and GaSb samples and interpret the physical meaning of these parameters. In this part, we use several methods to estimate the critical radius and use the data of hollow core radius to estimate other important growth parameters like the specific surface energy and the supersaturation in the vapor phase. Finally we discuss the temperature effect and the anisotropy found in the shape of InAs and GaSb spirals.
2.1 BCF Theory

2.1.1 The concept of the kink and the background of BCF Theory

The first macroscopic theory of crystal growth was constructed by Gibbs, etc. about a century ago. Within this framework, only macroscopic thermodynamic quantities were used. The microscopic elementary process of the attachment and detachment of building units (atoms or molecules) was not taken into account until 1927 when Kossel and Stranski introduced the concept of kink. The modern theory of crystal growth was thus developed.

Let's consider the (100) surface of a simple cubic crystal in a supersaturated ambient. Fig. 4 shows all the possible sites an adatom can occupy on the surface.
During growth, an adatom attaches to one of these sites and becomes part of the bulk crystal. Let's investigate all these sites. Site 1 represents a pit on the surface. Although it is the most energy favorable site for an adatom to attach to, such pits are very rare. Once all the pits on the surface are filled, there will be no more pits available because five bonds have to be broken for the generation of one pit. Thus, site 1 process is not probable because it cannot occur continuously. Site 2 represents a pit into the step
edge. Site 2 is not a probable site for growth for the same reason as that of site 1. Site 5: the adatom here is weakly bound and does not incorporate into the crystal. Site 4: this site has 2 bonds, but the adatom is still weakly bound and mobile at finite temperatures. Site 3: this is the so-called kink site. BCF theory has shown that at finite temperatures, there is a high concentration of kink sites i.e. a perfectly straight step becomes roughened by kink formations. Adatoms which attach here form 3 bonds and become rigidly locked to crystal. Also, an adatom coming from the vapor causes no change to the total surface energy because it fills three unsaturated dangling bonds and generates another three unsaturated dangling bonds after each attachment. In other words, site 3 attachment is a self-generating process: another site 3 is generated after each attachment in contrast with site 1 attachment which is self-terminating. Here, unlike all the other possibilities, the binding energy is equal to the association energy of three bonds, which is half of the total bulk bond energy. Hence, a kink position is also called a half crystal position. For more details, see ref. [14].
2.1.2 Mobility of adsorbed molecules on a crystal surface

Sections 2.1.2 through 2.1.5 summarize in condensed form the overall theory of the original BCF picture of crystal growth from the vapor. For more details, the reader is encouraged to read the original BCF paper [6]. The process of growth of a crystal surface with steps will be the result of three separate processes: (see Fig. 5) (i) exchange of molecules between the adsorbed layer and vapor, (ii) diffusion of adsorbed molecules towards the steps and exchange with them, and (iii) diffusion of adsorbed molecules in the edges of the steps towards the kinks and exchange with them.
Let $n_{s0}$ be the equilibrium surface concentration of adsorbed, mobile molecules:

$$n_{s0} = n_0 \exp(-W_s/kT) \quad (1)$$

where $W_s$ is the energy of evaporation from the kinks on to the surface; $n_0$ is the number per cm$^2$ of molecular positions on the surface; $k$ is Boltzmann's constant and $T$ the temperature.
The diffusion length $x_s$, which is the mean displacement an adsorbed molecule can make on the surface before being evaporated again into the vapor is defined by Einstein formula:

\[ x_s^2 = D_s \tau_s \]  

(2)

where $D_s$ is the diffusion coefficient and $\tau_s$ the mean lifetime of an adsorbed molecule. The Einstein formula can be derived from diffusion theory. Recall that the probability $dP$ that a molecule found at $x=0$, $y=0$, $t=0$ will be found between $x$ and $x+dx$, $y$ and $y+dy$ at time $t=t$ is:

\[ dP = \frac{1}{(4\pi D_s t)^{1/2}} \exp\left(-\frac{x^2+y^2}{4D_s t}\right) dx dy. \]

$x_s^2$ can be obtained by $x_s^2 = \int_{-\infty}^{\infty} dP(x^2 + y^2)$ with $t = \tau_s$. The result of the integral is equation (2).

For simple molecules we have:

\[ D_s = a^2 v' \exp(-U_s/kT) \]  

(3)

\[ 1/\tau_s = v \exp(-W'_s/kT) \]  

(4)

where $U_s$ is the activation energy between two neighboring equilibrium positions, $a$ the distance between them, and $W'_s$, the evaporation energy.
from the surface to the vapor. In general, when a molecule is adsorbed on the surface, the first step is physical adsorption where the interaction energy is several tenths of one electron volt (eV). The physically adsorbed molecule can move on the surface (hopping) because it is not strongly bonded. When it finds a kink, it will have a probability to form chemical bonds with the bulk molecules at the kink and become chemically adsorbed. The interaction energy of chemical adsorption is equal to the energy of a chemical bond which is several eV. Thus we can say that $W_s'$ is the energy of physical adsorption and $W_s$ the energy of chemisorption. $v$ and $v'$ are both of the order of the atomic frequency of vibration ($v \sim 10^{13}$ sec$^{-1}$). Assuming $v \sim v'$ and using (3) and (4), (2) becomes

$$x_s = a \exp\left\{ \frac{(W_s' - U_s)}{2kT} \right\}$$

(5)

BCF postulates that $W_s' > U_s$. We therefore have $x_s > a$, which is the condition that surface diffusion be important.
2.1.3 The rate of advance of a straight step

The supersaturation $\sigma$ in the vapor is defined as:

$$\sigma = \alpha - 1, \alpha = \frac{p}{p_0} \quad (6)$$

where $p$ is the actual pressure, $p_0$ the saturation or equilibrium value, and $\alpha$ is called the saturation ratio. $\sigma$ and $\alpha$ are assumed to be constant above the surface in the BCF picture. The supersaturation $\sigma_s$ of adsorbed molecules on the surface, which in general depends on position is defined as

$$\sigma_s = \alpha_s - 1, \alpha_s = \frac{n_s}{n_{s0}} \quad (7)$$

where $n_s$ and $n_{s0}$ are the actual and equilibrium concentration of adsorbed molecules respectively.

By the diffusion theory, the flux $j_s$, which is equal to the number of adatoms going into the step per unit length per unit time reads:
\[ j_s = -D_s \nabla n_s = D_s n_{s0} \nabla \psi \]  \hspace{1cm} (8)

where \( \psi \) is defined as \( \sigma - \sigma_s \), and \( j_s \) is the current on the surface. There will also be a current \( j_v \) going from the vapor to the surface: (for a derivation see the Appendix):

\[ j_v = (\alpha - \alpha_s) \frac{n_{s0}}{\tau_s} = n_{s0} \psi / \tau_s \]  \hspace{1cm} (9)

where \( \tau_s \) is the mean life of an adsorbed molecule on the surface. As molecules cannot be generated or annihilated, the continuity equation \( \nabla \cdot j_s = j_v \) must hold. Assuming \( D_s \) is independent of direction on the surface and using Einstein's formula and (8), (9), this equation can be written as:

\[ x_s^2 \nabla^2 \psi = \psi \]  \hspace{1cm} (10)

The next thing is to put in the boundary condition to solve this differential equation. At a typical temperature (room temperature or higher), BCF have shown that the average distance \( x_0 \) between two kinks along the step will always be much smaller than the diffusion length \( x_s \). Therefore the concentration near the step should be maintained equal to the equilibrium value as long as the exchange between the kinks and the surface is very rapid. Thus the boundary condition should be \( \sigma_s = 0 \) near
the step and \( \sigma_s = \sigma \) far from it. The differential equation has a simple solution:

\[
\psi = \sigma \exp(\pm y/x_s)
\]  

(11)

where \( y \) is the distance to the step, with the plus sign being used for \( y < 0 \) and the minus sign being used for \( y > 0 \). Now the current \( j_s \) can be obtained from (8) using (11) and putting \( y = 0 \). The velocity \( v_\infty \) which is equal to the rate of the increase of terrace width can be obtained by \( j_s/n_0 \), where \( n_0 \) is the number of atoms per unit area. Using (1),(2),(4),(8) and defining \( W = W_s + W_s' \) being the total evaporation energy, \( v_\infty \) can be written as:

\[
v_\infty = 2\sigma x_s v \exp(-W/kT)
\]  

(12)

The factor 2 arises by considering the currents coming in from both sides. This factor should be removed if the adatom incorporation only proceeds from one side of the step.

2.1.4 The rate of advance of a curved step

The above derivation is based on the assumption of an infinitely large nucleus or the straight step edge. In the practical case, the mean
evaporation energy of an atom from a finite size nucleus to the surface will be smaller. This can be understood as follows. Consider a crystal disk of one monolayer height with radius \( \rho \) sitting on the surface. Assume the crystal has a simple cubic structure with lattice constant \( a \). Recall that \( W_s \) is equal to the evaporation energy per molecule from a kink to the surface in a straight step, and let \( \gamma_o \) be the specific edge energy. Then the total energy of formation of the disk reads: 
\[
E_i = W_s \left( \frac{\pi \rho^2}{a^2} \right) - 2\pi \rho \gamma_o / a.
\]
Now we calculate the energy of evaporation \( W_s(\rho) \) per molecule from this disk. Let the radius decrease by \( d\rho \), which corresponds to the evaporation of \( dN = 2\pi \rho d\rho / a^2 \) atoms at the outmost ring of the disk. The change of total energy of formation is 
\[
dE_i = W_s 2\pi \rho d\rho / a^2 - 2\pi d\rho \gamma_o / a.
\]
\( W_s(\rho) \) can be obtained by \( dE_i/dN \), which is equal to \( W_s - \gamma_o a / \rho \). This means the atoms in a finite size island are less strongly bonded compared with the atoms in the bulk or an infinitely large island. This result was first derived by Gibbs-Thompson for macroscopic systems. It essentially represents the size dependence of the bulk and surface energies.

Now we go back to BCF theory. The supersaturation of the surface at the step \( \sigma_s(\rho) \) can be found using statistical mechanics: 
\[
\sigma_s(\rho) = \]
\[ \exp\{-W_s(p)/kT\}/\exp\{-W_s/kT\} - 1 = \exp\{\gamma_s a/(\rho KT)\} - 1. \]

In order to grow, we should have \( \sigma_s(p) \leq \sigma \), where \( \sigma \) is the supersaturation of the vapor phase. From this condition we obtain the minimum \( \rho \) which is called the critical radius \( (\rho_c) \) for a nucleus to grow. Letting \( \sigma_s(\rho_c) = \sigma \), we get:

\[ \rho_c = \frac{\gamma_s a}{kT \ln(\alpha)} \quad \alpha = \sigma + 1 \quad (13) \]

For near equilibrium growth, \( \sigma \) is small and \( \rho_c \) can be simplified as:

\[ \rho_c = \frac{\gamma_s a}{kT \sigma} \]

Next we will solve the differential equation (10) and find the step growth velocity. Recall equation (10): \( x_s^2 \nabla^2 \psi(r) = \psi(r) \), where \( \psi(r) = \sigma - \sigma_s(r) \). The boundary condition now is \( \psi(\rho) \). The solution of this equation is

\[ \psi(r) = \psi(\rho)\{I_0(\rho/x_s)/I_0(\rho/x_s)\} \quad (\text{for } r < \rho) \quad (14) \]

\[ \psi(r) = \psi(\rho)\{K_0(\rho/x_s)/K_0(\rho/x_s)\} \quad (\text{for } r > \rho) \quad (15) \]
where $I_0$ and $K_0$ are zeroth order Bessel functions of the first and second kind and

$$ \psi(\rho) = \sigma - \sigma_s(\rho) = \sigma - \{\exp(\gamma a/\rho kT) - 1\}.$$  

The current goes into the nucleus is $j = 2\pi \rho D_s n_{s0}(\partial \psi / \partial r)_{r=\rho}$. Using the formulae: $I_0'(z) = I_1(z)$, $K_0'(z) = -K_1(z)$, $I_0(z)K_1(z) + I_1(z)K_0(z) = 1/z$ and the expressions for $x_s$, $\tau_s$ and $n_{s0}$ given by (2), (4), (1), the radial velocity, $v(\rho) = j(\rho)/2\pi \rho n_0$, is therefore:

$$ v(\rho) = x_s^2 \exp(-W/kT) \psi(\rho) / \{ \rho I_0(\rho/x_s)K_0(\rho/x_s) \} \quad (16) $$

In the regime of non-overlapping diffusion fields in which the diffusion length $x_s$ is very small and $\rho > x_s$ is satisfied, we can use the approximation $I_0(\rho/x_s)K_0(\rho/x_s) = x_s^2/\rho$, then (16) becomes

$$ v(\rho) = v_\infty (\alpha - \alpha^{pc/\rho}) / \sigma \quad \text{and if } \sigma \text{ is small, } v(\rho) \text{ can be simplified:} $$

$$ v(\rho) = v_\infty (1 - \rho_c/\rho) \quad (17) $$

The physical meaning of (17) is very clear: for an infinitely large nucleus ($\rho = \infty$) the step grows the fastest; for a nucleus whose radius is smaller than $\rho_c$ the step has a negative growth velocity which means evaporation and no growth.
2.1.5 $\rho_c$ in non-overlapping and overlapping diffusion fields

Let's consider a straight step edge ended with a screw dislocation. At the beginning, the growth velocity is almost the same for each point along the step edge except the dislocation center point. This velocity distribution results in the winding in of the initially straight step and the forming of a spiral. As the winding in proceeds, the center part of the spiral becomes more and more curved until the radius of curvature there is equal to $\rho_c$. At that moment, the surface supersaturation at the center ($\sigma_s$) is equal to the supersaturation of the vapor phase ($\sigma$) and no more winding in is possible because $\sigma_s$ can't be larger than $\sigma$. Thus after that moment, the distribution of radii of curvature along the spiral as well as the shape of the spiral will be stabilized. The growth front of the spiral after stabilization can be obtained by the rotation of the "rigid spiral" with a constant angular velocity $\omega$. (see Fig. 6)
Figure 6 The process of winding in and then getting a steady shape. $T$ is the time scale in this simulation. There is a feedback effect between the shape of the step and the growth velocity. The result is a stationary shape of spiral rotating steadily after the initial winding in [44].

BCF first investigated the stabilized spiral morphology in the regime of non-overlapping diffusion fields. In this regime, the surface diffusion length $x$, is very small and one can use the expression $v(\rho)=v_0(1-\rho_0/\rho)$ for velocity. The dependence of radius of curvature $\rho$ on the point $(r,\theta)$ is given by:
\[ \rho = (1 + r^2 \theta^2)^{3/2}/(2\theta' + r^2 \theta^2 + r\theta'') \]  \hspace{1cm} (18)

If the angular velocity of the whole spiral is \( \omega \), then the normal velocity at the point \((r, \theta)\) is:

\[ v(r) = \omega r (1 + r^2 \theta^2)^{-1/2} \]  \hspace{1cm} (19)

Put (18) and (19) into (17). The approximation can be done in the following way: for small \( r \) one neglects \( r^2 \); for large \( r \) one neglects \( 1/r^2 \). So the equation is simplified for these two cases:

for \( r \to 0 \): \( \theta' = 1/(2\rho_c) - \omega r/(3\rho' \rho_c) \)  \hspace{1cm} (20)

for large \( r \to \infty \): \( \theta' = (\omega / \rho') (1 + \rho_c / r) \)  \hspace{1cm} (21)

Now choosing a general form \( \theta' = a + b/(1 + c r) \) and determining \( a, b, c \) in such a way that this general form reduces to (20) and (21) under those two extreme conditions, we get the shape:

\[ \theta = 3^{1/2}/2(1 + 3^{1/2}) \{ r/\rho_c + \ln(1 + r/(3^{1/2} \rho_c)) \} \]  \hspace{1cm} (22)

\[ \omega = 3^{1/2} \rho' / (2 \rho_c (1 + 3^{1/2})) = 0.63 \rho' / 2 \rho_c \]  \hspace{1cm} (23)
The distance \( y_0 \) between successive turns of the spiral at large \( r \) is given by: \( y_0 = 2\pi/\theta_{\infty}' = \{4\pi/0.63\} \rho_c = 19.95 \rho_c \). A better approximation was done later [9] to modify 19.95 to 19. This is called the 19p\(_c\) result.

In the derivation of the 19p\(_c\) result, BCF theory assumes that after the spiral becomes stable, the radius of curvature at the center is \( \rho_c \) and the surface supersaturation(\(\sigma_c\)) at that point is equal to the supersaturation of the vapor phase which is a constant, i.e. \( \sigma \). So there is no surface flux going into the center.

In the preceding analysis, it was assumed that the diffusion length is very small compared with the step spacing and that each step moves independently of the other. We now consider the case of high supersaturation or large \( x_s \), where the key assumption of BCF theory breaks down. We call this the overlapping diffusion fields regime. For historical reasons the growth in this regime was described by the so-called "back force" theory. The idea is to approximate the first turn of the spiral by a circular step with radius \( \Lambda_0 \) [44] (See Fig. 7).
Recall equation (14): \( \psi(r) = \psi(\rho) \left\{ I_0(\rho/x_o) / I_0(\rho/x) \right\} \) (for \( r < \rho \)) where \( \psi(r) \) is equal to \( \sigma - \sigma_s(r) \). Now \( \rho \) is equal to \( \Lambda_0 \) and \( \psi(\rho) \) is the \( \psi \) value at the first turn step edge, so we have: \( \psi(\rho) = \psi(\Lambda_0) = \sigma \) because the surface supersaturation at the step edge is zero. We can find the surface...
supersaturation at the center by putting $\sigma_s(r=0) = \sigma_{s0}$ into that equation and find
the expression of $\sigma_{s0}$: (Bessel function $I_0(x=0)$ is equal to one)

$$\sigma_{s0} = \sigma \left\{ 1 - 1/I_0(\Lambda_0/x_s) \right\}$$  \hspace{1cm} (24)

As $I_0(x>=0)$ is a monotonically increasing function with $I_0(0)=1$, the surface supersaturation at
the center is always smaller than $\sigma$. This means the actual radius of curvature at the center, $\rho(0)$ should be larger than $\rho_c$. Recalling $\sigma_s(\rho) = \exp(\gamma a/\rho kT) - 1$, using the approximation $e^x = 1 + x$ when $x$ is small (near equilibrium case) and noticing $\sigma_s(\rho_c) = \exp(\gamma a/\rho_c kT) - 1 = \sigma$ and $\sigma_s(\rho(0)) = \exp(\gamma a/\rho(0)kT) - 1 = \sigma_{s0}$, we get:

$$\rho_c = \rho(0) \left\{ 1 - 1/I_0(\Lambda_0/x_s) \right\}$$  \hspace{1cm} (25)

From (24) and (25), we find that when $x_s$ is much smaller than $\Lambda_0$, $\sigma_{s0}$ and $\rho(0)$ are approximately equal to $\sigma$ and $\rho_c$. This means in the regime of non-overlapping diffusion fields, the assumption: $\rho(0) = \rho_c$ in BCF theory is reasonable and the 19$\rho_c$ result is applicable.

In the BCF picture, as $\sigma$ increases, the step spacing decreases. The diffusion fields start to overlap when $19\rho_c = 2x_s$. The factor of 2 is absent.
if there is only diffusion from one side of each step. This occurs at a critical supersaturation of $\sigma_c = 19\gamma\Omega/(2kT\chi_s)$, where $\Omega$ is the growth unit volume and the factor $2'$ is again optional. In the regime of overlapping diffusion fields, $v(\rho)$ is no longer equal to $v_-(1- \rho_c/\rho)$ and the $19\rho_c$ result is certainly not right.

We are now interested in very high supersaturation $\sigma >> \sigma_c$ in which there is strong over-lapping of diffusion fields. At the center of the spiral, we again have:

$$\rho_c = \rho(0) \{ 1 - 1/I_0(\Lambda_0/x_s) \} \tag{25}$$

Using $1/I_0(x) \sim 1 - x^2/4$ for small $x$, we obtain:

$$\rho_c = \rho(0)\Lambda_0^2/4x_s^2 \tag{26}$$

Recall that in this expression, $\Lambda_0$ represents the radius of a circle which approximates the first turn, $\rho(0)$ is the radius of the curvature at the center of the actual spiral. If we assume that actual spiral is Archimedean, then it can be shown that: $4\pi\rho(0) = \Lambda_0$. Put this into equation (26), we get:

$$\rho_c = \Lambda_0^3/(16\pi x_s^2) = \Lambda_0^3/(50x_s^2) \tag{27}$$
This gives another estimate for \( \rho_c \), given a knowledge of \( \kappa \). Van der Eerden [13], using a more exact approach showed that the outer turn spacing will differ from the central one by a factor of less than 2.

2.1.6 The prediction of closed loops

From the above picture, one can see that a dislocation center “sends out” loops of growth fronts in some way similar to a source sending out wave fronts. Now suppose we have two opposite sign dislocation centers on the surface with a distance larger than \( 2\rho_c \) (see Fig. 8).

Figure 8 The formation of closed loops of step when the distance between two opposite sign dislocation centers is large [6].
Growth fronts differ from wave fronts in the fact that when they meet they annihilate (see the dash lines in Fig. 8). As the growth fronts still keep the form of steps with the same height when they separate, the result will be closed loops of step. When the distance between two dislocation centers is smaller than $2p_c$, which means one of the dislocation centers is inside the first loop of the other, the formation of closed loops is impossible.

2.2 The theory of hollow dislocation core

For simplicity we consider the case of a screw dislocation in a material with isotropic elastic constants. Then the shear strain at the surface of the cylinder is $b/(2\pi r)$, where $b$ is the magnitude of the Burgers vector of the screw dislocation, and $r$ the radius of the cylinder (See Fig. 9).
From mechanics we know there is a strain-energy density of $\mu b^2/(8\pi r^3)$, where $\mu$ is the shear modulus. We assume that the strain is linear, which will be shown to be the case in our samples. Suppose now a unit length of shell of a differential thickness $dr$ evaporates and deposits elsewhere resulting in the formation of unstrained crystalline material. The interior cylindrical surface is thus enlarged. If $\gamma$ is the specific surface free energy.
of the substrate, the total increase in free energy per unit length of cylinder 
dG contains three terms [11]. The first term dG(i) which considers the 
transformation of strained into non-strained crystalline material is equal to 
\[ -u(r)2\pi r dr \], where \( u(r) \) is the strain energy density. For the spirals found in 
our samples, the magnitude of Burgers vector (10 Å to 36 Å) is much less 
than the hollow core radius (120 Å to 870 Å, proportional to the magnitude 
of Burgers vector). The strain at the core wall, which is equal to the 
magnitude of Burgers vector divided by the hollow core circumference, is 
very small and we can use the elastic approximation \[ \mu b^2/(8\pi r^2) \] for \( u(r) \). 
The second term dG(ii) which considers the transformation of non-strained 
crystalline material into supersaturated material is equal to 
\[ (kT\sigma/\Omega)2\pi r dr, \] where \( \sigma \) is the supersaturation in vapor phase and \( \Omega \) the volume of one 
adsorbed molecule. The third term dG(iii) considering the increase of area 
of the cylinder is equal to \[ 2\pi \gamma dr \], where \( \gamma \) is the specific surface free 
energy. We can obtain the hollow core radius \( r_{hc} \) by solving 
\[ dG = dG(i) + dG(ii) + dG(iii) = 0. \] Frank [10] considered only dG(i) and dG(iii) and 
obtained a hollow core radius \( r_0 = \mu b^2/(8\pi^2\gamma) \) which is called Frank radius. 
If one consider all the three terms [11], the hollow core radius will be:
Fig. 10 shows a vertical metalorganic chemical vapor deposition (MOCVD) reactor. A more realistic drawing of the MOCVD setup will be
presented in the experimental section of this thesis. Organometallic compounds (precursors) such as trimethylindium (TMI) and tertiarybutylarsine (TBA) are transferred into the chamber by passing H₂ carrier gas through the two bubblers shown in Fig. 10. The flux rate as well as the partial pressure of H₂ carrier gas is much much larger than those of the precursor's. The total pressure in the chamber is always 50 Torr in our experiments. There are three reasons for using a carrier gas. The first is that it can push the precursors forward due to its large mole fraction. The second is that by using carrier gas one can control the gas composition in the vapor phase quickly. This is very useful for heterostructures in which the depth of each layer must be controlled accurately. The third is that it can reduce the surface oxides. There are two important reasons for choosing H₂ as a carrier gas. The first is that it can be easily purified by means of a palladium membrane. The second is that H₂ flow has a smaller Reynolds number (Reynolds number : \( R_e = \frac{\rho V d}{\eta} \), where \( \rho \) is the density, \( V \) the average flow speed, \( d \) the diameter of the tube, \( \eta \) the coefficient of viscosity) compared with other gases. When \( R_e \) is small (less than 100) the flow is laminar. For laminar flow each element of the reactive species travels smoothly along a well defined path [14] and
each element starting at the same place follows the same path. Laminar flow is preferred over turbulent flow since the latter results in longer gas residence times.

The organometallic compounds are thermally decomposed above or on a substrate (e.g. GaAs) which is placed on a heated susceptor. There are two kinds of thermal decomposition (or pyrolysis). Homogeneous pyrolysis occurs totally in the vapor phase without the involvement of the vapor-crystal interface, while heterogeneous pyrolysis needs the interface to play an important catalytic role. Experimental evidence showed that the pyrolysis of the group III compound is homogeneous [15] and the pyrolysis of the group V compound is heterogeneous [16]. The decomposed species lead to the growth of semiconductor through complicated surface reactions. The detailed physical process of these reaction are not clear yet.

Unlike MBE which involves the reaction of one or more thermal beams of molecules under ultra-high-vacuum (UHV) conditions, MOCVD is a hydrodynamic process. The boundary condition at the reactor walls
and the substrate, i.e. wherever the vapor encounters a solid surface, is that the velocity vector is zero. The velocity component perpendicular to the surface is zero since no flux across the boundary exits. The parallel component is constrained to be zero because of the friction between the gases and the surface. As a consequence of this boundary condition and the gas viscosity, the flow of the fluid parallel to the wall will be increasingly retarded as the wall is approached. This region of decreasing velocity is referred to as a boundary layer. Fig. 11 shows a boundary layer configuration for a vertical reactor.

*Figure 11* Velocity profile in a vertical reactor showing the existence of a boundary layer [17].
The velocity profile labeled by $U$ or $U_\infty$ in the Fig. 11 shows the decreasing of vertical velocity when the gases approach the substrate. The boundary thickness ($\delta$) is defined here as the distance from the interface at which the vertical velocity becomes 99% of its free stream value $U_\infty$.

Fig. 12 shows a schematic diagram of the temperature dependence of MOCVD growth rate found in experiment.

![Schematic plot of MOCVD growth rate vs. temperature](image)

*Figure 12 Schematic plot of MOCVD growth rate vs. temperature [18].*
Three important regions are generally observed: a decomposition limited region, a mass transport limited region, and a desorption limited region. In the first region (300-400°C for InAs growth), the growth rate is dominated by the fraction of the metalorganic compound being decomposed. In the intermediate region, which is the region normally used, all precursors are fully decomposed and the growth rate is independent of temperature because now the diffusion (mass transport) of precursors or their decomposed species through the boundary layer affects the growth rate most. When the temperature is higher than 750°C, the growth rate will decrease with increasing temperature due to desorption of reactants.

Another important aspect of III-V semiconductor growth using MOCVD is that in order to grow high quality samples, people use a large excess of group V source to prevent the formation of In or Ga droplets on the surface. The growth rate is therefore limited by the partial pressure of the group III elements.
Chapter 3. Experimental

3.1 MOCVD setup used for making our samples

Figure 13  MOCVD setup used in our lab.
Fig. 13 shows the MOCVD setup used to grow the samples studied in this thesis. Several programmable mass flow controllers (MFC) and electronic pressure controllers (EPC) are used to control the gas flow which is crucial to the quality of the growth. The mixing area is responsible for the mixing of the group III and group V precursors before they react on the surface. The two windows on the left and right side of the reactor are designed for the observation of the sample. During growth, the reactants may deposit on the windows. There are two hydrogen purge lines at the windows to prevent this. A third hydrogen line is used to maintain an outer flow of hydrogen parallel to the inner nozzle. The purpose is to keep the velocity profile constant inside the reactor. There is also an in situ reflectance difference spectroscopy (RDS) setup to monitor the growth [47].

3.2 Atomic Force Microscopy (AFM)

An atomic force microscope (AFM) is an opto-mechanical instrument, which can detect extremely small forces (~nN). Most AFMs have vertical resolution below 0.1 nm, whereas lateral resolution is around
10 nm. We use an AFM to measure semiconductor morphologies in order to extract important growth parameters. Fig. 14 shows the most important part of an AFM.

Figure 14 AFM = Probe Head + PZT Scanner + Electronics.

A laser beam emitted by a laser diode is reflected by a mirror and then by a cantilever which is attached to the back of an AFM tip. The AFM tip is a piece of pyramid-shaped silicon used to detect the tip-sample force. The light from the cantilever hits a position sensitive photodetector (PSPD).
which is made up of two identical Si photodetectors (called A and B detectors). To understand how an AFM works, three important things are worth being mentioned.

1) Fig. 15 shows a laser beam with a circular cross section of radius $R$. The dashed line is the boundary between the two photodetectors. The laser beam will hit A and B detectors with generally different light intensity. In the following text, A or B also refers to the light intensity on A or B. In general, the magnitude of $x$ will depend on the deflection of the tip, which in turn depends on the force applied to the cantilever.

![Figure 15](image_url)

*Figure 15* A laser beam with a circular cross section shining on the PSPD. The dashed line is the dividing line of the A, B detector. The shift $x$ is the distance from the circle center to the dividing line.
2) An AFM is composed of two main parts. The probe head consists of the laser diode, mirror, cantilever, and PSPD. The second part consists of a sample platform which is mounted on the top of a piezoelectric scanner tube (PZT). In our setup the sample oscillates on the PZT in the horizontal direction with a pre-determined range and frequency and the probe head responds to small changes in the height of the sample. Actually the x, y, z movements of a PZT are coupled because the strain components in the PZT are related to the stress components with a tensor. The bending of the cantilever by the tip-sample force will generate a change of the reflection angle which can be measured by \((A-B)/(A+B)\) if we assume no bending corresponds to "A=B" (the equilibrium position of the beam). In practice, \((A-B)\) used in an AFM is much less than \((A+B)\) so the shift \(x\) (see Fig. 15) of the beam from its equilibrium position will be very small. As the light intensity detected by the detector is approximately proportional to the area on the detector illuminated by the light, we use \((A-B)/(A+B) = 2\cdot x \cdot (2R)/(\pi R^2)\) to calculate \(x\) if the radius of the circle in Fig. 15 is \(R\). The reflection angle change \(\Delta \theta = x/D\), where \(D\) is the
distance from the cantilever to the PSPD. Fig. 16 shows the bending of a cantilever by the tip-sample repelling force between sample and tip.

Noticing that $\Delta \theta$ is equal to the bending angle of the cantilever, the cantilever bending length $\Delta Z$ ($\sim 3$ Å for one monolayer) is $L \cdot \Delta \theta$, where $L$ is the cantilever length which is about 100 µm for our AFM (See Fig. 16). From $\Delta Z$ and the force constant $k$ ($\sim 0.24$ N/m) of the cantilever which can
be found in the product manual [49], we can obtain tip-sample force which is equal to kΔZ.

![Diagram of force vs. tip-to-sample separation](image)

**Figure 17** Tip-sample force as a function of the separation between them.

3) Fig. 17 shows the force between tip and sample as a function of the distance between them. It should be noticed that at the end of an AFM tip, there are hundreds of atoms and the tip-sample force is the result of multi-atom interaction. When the tip is far away from the sample (the non-contact mode) the force is Van der Waals force which is attractive and weak. One the other hand, when the tip is very close to the sample (the contact mode), the force is repulsive and strong due to the charge-charge.
interaction. The AFM in our experiment always works in the contact mode. The magnitude of the bending length of the cantilever corresponds to the magnitude of the repulsive force which depends on the tip-to-sample separation.

Figure 18 How an AFM picture is generated [49].
Fig. 18 shows the process of how an AFM picture can be generated. During image acquisition the PZT scanner is always scanning. As to the vertical direction, we need to tell the control system a reference signal value of tip-sample force which corresponds to a certain magnitude of cantilever bending length and thus to a certain magnitude of tip-to-sample separation in the contact region. To begin the experiment, we first adjust the position of PSPD to make sure (A-B) is close to zero because there is no bending. Then we lower the probe head to approach the sample. When the tip-sample force between the tip and any point of the sample in the scanning range is close to the reference value within a certain range of tolerance, the approaching stops and the Z feedback loop begins to operate. Now the control system measures the actual (A-B) of each point of the sample and compare it with the reference value and generate an error signal. The error signal is equal to the result of actual (A-B) minus the reference value. The error signal is sent to the feedback electronics which generates a feedback voltage and then sends it to the PZT. This feedback voltage causes the PZT to extend or contract vertically (Z direction) to keep the tip-to-sample force near the reference value. When the feedback loop is optimized, the scanner's Z motion matches the surface
topography. The feedback signal can then be used to generate the image of the sample surface. The sample is now rastered in the x-y plane with a fixed force maintained by the feedback loop. The morphology information of the surface is generated by recording the piezo voltage at each point during the raster scan.

Our AFM is an Autoprobe CP type made by Park Scientific Instruments. Table 1 summarizes the typical AFM working conditions:

<table>
<thead>
<tr>
<th>Scanner</th>
<th>Scan rate</th>
<th>Tip-sample Force</th>
<th>Sample size</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 μm and 100 μm</td>
<td>0.5 to 10 Hz</td>
<td>4-10 nN</td>
<td>0.025 to 9 cm²</td>
</tr>
</tbody>
</table>

*Table 1 Typical working conditions of our AFM.*

Using a 5 μm scanner gives us better images but limits the scope of observation. On the other hand, using a 100 μm scanner gives us the overall morphology information on the surface. Thus, we use the 5 μm scanner when studying one spiral and use the 100 μm scanner when studying dislocation density on the surface.
3.3 Sample preparation

The samples studied in this thesis were grown by S. P. Watkins, C. A. Tran (InAs) and R. Ares (GaSb). Epilayers of InAs (GaSb) were grown on nominally exact [001] GaAs substrates. The procedure [24] consisted of the growth of a thin (about 100nm) buffer layer of InAs (GaSb) at 400°C (470°C) followed by the growth of a thick final layer at 540°C (670°C). The thin low temperature buffer layer buffers the lattice mismatch between InAs (GaSb) and GaAs to increase the quality of the final layer. Typical sample growth rates were between 0.5 to 1.0 nm/s.
Chapter 4. Data Analysis

4.1 Spiral formation and dislocation density

The InAs/(AlGa)Sb material system has great promise for the fabrication of high speed transistors. The lack of lattice-matched semi-insulating substrates has forced us to devote our studies to highly mismatched substrates such as InP(4% mismatch) and GaAs(7% mismatch). The stress between the substrate and the epilayer due to mismatch results in the formation of screw dislocations which propagate into the epilayer. Dislocations introduce charged traps and affect the reliability of optoelectronic devices, e.g. lasers. In order to observe well formed spirals, the dislocation density must be reduced sufficiently to permit the development of several turns. An effective way for reducing the dislocation density is to grow a thin low temperature buffer layer before the growth of the thick epilayer. Fig. 19 (a) and (b) compare the AFM images of epilayers grown at 540 C without and with buffer layer growth, respectively.
Figure 19 (a) and (b) compare AFM images of epilayers grown at 540° C without and with the two step growth method, respectively. The rms roughness are, respectively, 80 and 2.1 nm [24].
The root mean square (rms) roughness of the surface decreases from 80 nm to 2.1 nm after using the buffer layer method. Also, the introduction of buffer layer greatly reduces dislocation density. Thus, the dislocation density values of our samples are as low as $10^6$/cm$^2$-$10^7$/cm$^2$ compared with $10^{11}$/cm$^2$-$10^{12}$/cm$^2$ for samples without using the buffer layer method [45]. Low dislocation densities are necessary for the observation of well formed spirals because of the weaker interference between spirals. Figs. 19 (c) to (a) show how the dislocation density decreases and how the spirals become more and more well-resolved when the thickness of the InAs epilayer increases from 0.5μm to 10μm. (It should be pointed out that Fig. 20 and almost all the AFM images shown afterwards have been flattened in order to get better contrast. In the line-by-line flattening, the best fit to each individual height profile is made and then subtracted, one line at a time). With increasing epilayer thickness, more and more spirals will annihilate and only those spirals which are more isolated from other spirals survive and develop into well formed spirals. We also found in our growth that in order to obtain the spiral morphology, we cannot choose substrates with relatively large miscuts, for example, miscuts of the order of a couple of
degrees. In that case, the step density due to the miscuts is very high which results in a completely different surface morphology [25].

Figure 20 Spiral morphology and epilayer thickness.

Dislocation density is a very important factor in the fabrication of devices. We can use AFM as a quantitative tool for measuring dislocation densities under certain conditions. Fig. 21 shows a comparison of 100µm scans for thick layers of InAs and GaSb grown at temperatures of 540°C and 580°C respectively on GaAs [001] substrates.
From the images above, we can see that the surfaces of both samples consist of hillocks whose sizes have a certain distribution. Using AFM the maximum peak-to-valley height and root-mean-square (rms) roughness for InAs are measured to be 13 nm and 1.8 nm respectively. For the GaSb surface, the corresponding numbers are 38 nm and 5 nm. We also find from the images that GaSb has a much smaller hillock density than InAs although the former has a larger roughness. Fig. 22 (a) and (b) show details of a typical hillock picked out from the hillocks shown in Fig. 21 (a) and (b) respectively.

Figure 21 Comparison of large scale surface morphology of a 10μm InAs epilayer on GaAs (a) (sample: InAs 426) and a 5μm GaSb epilayer on GaAs (b) (sample GaSb 714), showing dislocation induced hillocks.
(The caption of the above figure is on the next page.)
Figure 22 Higher magnification views of InAs (a) and GaSb (b) morphology.

The spirals are generated by the winding in of step edges ending with screw dislocations. The magnitude of Burgers vector can be obtained by counting how many branches exist in the spiral. For example, the Burgers vectors for Fig. 22 (a) and (b) are \( n=4 \) and \( n=3 \) monolayer height respectively. The screw dislocation density can be estimated by simply counting the number of hillocks in a number of AFM images. This method has recently been used to count the screw dislocation densities in InAs [25]. Table 2 is a summary of dislocation density as a function of substrate material, epilayer thickness,
and temperature. Low temperature buffer layer method is used for all these samples.

<table>
<thead>
<tr>
<th>Epilayer</th>
<th>Substrate</th>
<th>Growth Temperature(°C)</th>
<th>Epilayer thickness (μm)</th>
<th>Dislocation Density(cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InAs426</td>
<td>GaAs</td>
<td>540</td>
<td>10</td>
<td>5x10⁶</td>
</tr>
<tr>
<td>InAs787</td>
<td>GaAs</td>
<td>540</td>
<td>2.5</td>
<td>2.5x10⁷</td>
</tr>
<tr>
<td>InAs640</td>
<td>GaAs</td>
<td>540</td>
<td>0.5</td>
<td>2-10x10⁸</td>
</tr>
<tr>
<td>InAs</td>
<td>InP</td>
<td>540</td>
<td>10</td>
<td>1x10⁶</td>
</tr>
<tr>
<td>InAs</td>
<td>InP</td>
<td>540</td>
<td>5</td>
<td>3x10⁸</td>
</tr>
<tr>
<td>InAs</td>
<td>InP</td>
<td>540</td>
<td>2.5</td>
<td>3x10⁶</td>
</tr>
<tr>
<td>InAs</td>
<td>InP</td>
<td>540</td>
<td>0.5</td>
<td>2-10x10⁸</td>
</tr>
</tbody>
</table>

** The above measurements are from ref. [25]

*Table 2 Dislocation density versus epilayer material, substrate material, growth temperature and epilayer thickness.*

4.2 Monomolecular layer height and multi-branch

The measurement of step height is based on the working mechanism of AFM cantilever. The monolayer height along the [001] direction of a III-V compound is determined by its zincblende structure to be half the lattice constant which is approximately 3.0Å for both InAs and GaSb. Our measurements show that all the steps are of monomolecular height as opposed to multiple layer or "bunched" steps. Fig. 23 shows the procedures of step height measurement: (1) draw a short line across the
step edge. This gives us the height profile along the line. Notice that the height profile across the step edge is a ramp instead of being a straight vertical line. Because the tip has hundreds of atoms detecting the repulsive force from the surface, the magnitude of the total force will change gradually between the tip starting passing and finishing passing the step edge. With this picture in mind, we can expect that the slope of the ramp should decrease when the tip becoming more and more blunt which is true experimentally. (2) put one marker at the upper edge of the step. (3) put the other marker at the lower edge of the step and read the height. Fig. 24 shows the measurement of the step height on a GaSb sample which gives a height of 3.1 Å.
Figure 23 The procedures of the measurement of the step height on an InAs Sample.
Figure 24 The measurement of the step height on a GaSb sample.

This result does not change with the location of the step or from sample to sample. Other researchers observed only single monolayer steps
in the study of the spiral morphology of III-V compounds grown by MOCVD or MBE [26] [27] [28] [29]. It is easy to understand the reason for monomolecular step height within the BCF picture. In BCF theory, a step grows by the surface diffusion of adatoms. It is very unlikely for the formation or growth of a step of several monolayer heights because this implies one adatom will climb on the shoulder of the other. The same argument can explain why, for example, in Fig. 22 (a) we have four branches of spiral with Burgers vector one instead of one branch of spiral with Burgers vector four. Fig. 25 shows schematically the time evolution of a step of four monolayer height initially.

Figure 25 Time evolution of a step of initially four monolayer heights.
The bottom layer has highest flux so the terrace above it grows very rapidly, reducing the flux into the bottom. In other words, wide terraces shrink, and narrow terraces grow, resulting in stable equally spaced terraces. This argument assumes that adatoms only attach to "uphill" edges, i.e. downhill edges are repulsive.

4.3 The critical radius

From the theoretical section 2.1.4, we know that the critical radius is a measure of how difficult it is for a small crystal island to grow instead of being evaporated. It is also the minimum value of the radius of curvature of a step that will attract adatoms and grow. In other words, the maximum curvature on a step will approach the inverse of the critical radius. In BCF theory, the most curved place is at the starting point of a spiral (the dislocation center). In practice, the curvature at this point is hard
to measure. Nevertheless, the critical radius can be estimated in several ways based on BCF theory.

Fig. 26(a) shows the verification of Frank's prediction which claims that when the distance between two opposite sign dislocation centers is larger than two times the critical radius, closed loops will form. We can thus use the distance between two dislocations to estimate the upper limit of the critical radius. From the measurement on Fig. 26(a), we conclude that the critical radius of InAs sample is less than 100 nm.

Fig. 26(b) shows a pair of dislocations of opposite sign. In this case, the separation is much larger than two times the critical radius, allowing each dislocation to wind up into well formed spiral. Note the annihilation of steps between the dislocation centers.
In the non-overlapping diffusion fields regime, an estimate of critical radius can be obtained by the "19ρc" resulting from BCF theory which gives the inter-step spacing far away from the dislocation center. Fig. 27 and 28 show typical measurements to estimate the ρc value of InAs. We notice that the spiral has an elliptical shape. The major axis and minor axis of the ellipse are oriented along the [110] and the [110] directions respectively. (see section 4.7 for a discussion of anisotropy) We have done such measurements on several spirals for sample InAs 426, and the results are summarized in Table 3. These data give an estimate of 19.5
± 3 nm for the critical radius of InAs under the growth condition stated in Table 2.

Figure 27 The measurement of the interstep spacing far away from the center of an InAs spiral along [110].
Figure 28 The measurement of the interstep spacing far away from the center of an InAs spiral along [110].

<table>
<thead>
<tr>
<th>InAs spiral</th>
<th>y₀ [1 1 0] direction nm</th>
<th>y₀ [1 1 0] direction nm</th>
<th>avg (2 directions)</th>
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<tr>
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<td>352</td>
<td>499</td>
</tr>
<tr>
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<td>380</td>
</tr>
<tr>
<td>#4</td>
<td>313</td>
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<td>#5</td>
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<td>255</td>
<td>331</td>
</tr>
<tr>
<td>#6</td>
<td>515</td>
<td>231</td>
<td>345</td>
</tr>
<tr>
<td>average</td>
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</tr>
<tr>
<td>deviation</td>
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<td></td>
<td>62</td>
</tr>
</tbody>
</table>

Table 3 Measurements of far-from-center inter-step spacing for InAs.
In Fig. 29, 30 and Table 4, we do similar measurement for a GaSb spiral of Burgers vector 3. Again we see a similar anisotropy in the step spacing, which we discuss in section 4.7. From section 4.7, we know that the horizontal and vertical axes in Figs 30 and 31 are along the [\(1\overline{1}0\)] and [\(1\overline{1}0\)] directions respectively. From these measurements, the critical radius for GaSb is estimated to be \(23.4 \pm 0.4\) nm for the present growth conditions. Again in the above pictures, we should notice the image flattening is responsible for no net vertical change in the height profile across several steps.
Figure 29 The measurement of the interstep spacing far away from the center of a GaSb spiral along [110].
Figure 30 The measurement of the interstep spacing far away from the center of a GaSb spiral along [1 1 0].

<table>
<thead>
<tr>
<th>GaSb spiral</th>
<th>( y_0 ) [1 1 0] direction nm</th>
<th>( y_0 ) [1 1 0] direction nm</th>
<th>avg (2 directions)</th>
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<td>436</td>
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<tr>
<td>#2</td>
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</tr>
<tr>
<td>deviation</td>
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<td>7.6</td>
</tr>
</tbody>
</table>

Table 4 Measurements of far-from-center inter-step spacing for GaSb.
The $19\rho_c$ result assumes that the surface diffusion length is much smaller than the interstep spacing. On the other hand, in the overlapping diffusion fields regime, the critical radius should be estimated by the formula $\rho_c = (1/50) \Lambda_0^3/x_s^2$, where $\Lambda_0$ is the interstep spacing as shown in section 2.1.5. Since we do not have a firm estimate of $x_s$, we can only obtain a lower bound for $\rho_c$ by using a maximum reasonable value for $x_s$ of approximately 500 nm. This estimate is based on the fact that terrace widths of greater than 500 nm are never observed in our system for GaAs or InAs over a wide range of growth conditions. This reduces the estimates of $\rho_c$ to 3.6 nm and 7.3 nm for InAs and GaSb respectively.

The reader may have noticed, that in Fig. 22, the inter-step spacing of the first turn is much larger than those of the others. This feature is common and may be explained by the strong strain field near the dislocation center. The strain field tends to make the atoms less, strongly bonded as the finite size effect does (see section 2.1.4). We know that in the non-overlapping diffusion fields regime, the finite size effect will decrease the velocity of step advancement from $v_-$ to $v_-(1- \rho_c/\rho)$, where $\rho$ is the radius of curvature at the point of interest. Similarly, if we consider
the strain effect, the velocity of step advancement will be further decreased to
\( v_s(1-\rho_c/\rho-r_0\rho_c/r^2) \), where \( r_0 \) is the Frank radius (see section 2.2) and \( r \) the
distance between the dislocation center and the point of interest. (For a
derivation of this formula, see ref. [32]) From this expression, we can see
that the velocity of step advancement is constant far from the center, and
quickly decreases near the center. As a result, the inner step edge of the
first turn will advance much slower than the outer one. For other turns, \( r \) is
so large that the inner step edge advances almost as fast as the outer one.
Thus, under this velocity profile, the spiral should have a wider first turn.
Computer simulations using this velocity formula did obtain a wider first
turn and confirmed the above explanation. [41]

Land et al. [30] suggested another way to estimate the critical
radius. Because the value of \( \rho_c \) is bounded by the maximum value of
curvature of the steps, they estimate \( \rho_c \) by a large number of measurements
of the radius of curvature of small capes (any convex portion of a step).
Using this approach, we have measured the radii of curvature at various
locations on a thin epilayer sample. We choose a thin epilayer sample
because most dislocations on it have not developed into large spirals yet.
Fig. 31 shows such a measurement on an InAs sample with growth conditions similar to that of the spiral shown in Fig. 27 and 28.

Figure 31 Estimate of the critical radius by measuring the radii of curvature of capes. (The size of this image is 5 μm by 5 μm)

The numbers on the figure are the indexes of the capes. As we can read the coordinate of any point on the figure, we can therefore use a numerical
method to find out the minimum radius of curvature of each cape. The results of such measurements and calculations are collected in Table 5. From this result, we conclude that the critical radius of InAs should be less than 35 nm. In other word, the estimation by the "19ρc" method is reasonable.

<table>
<thead>
<tr>
<th>Location</th>
<th>1</th>
<th>2</th>
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<th>7</th>
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<td>94</td>
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<td>50</td>
<td>61</td>
<td>67</td>
<td>39</td>
<td>43</td>
<td>35</td>
<td>36</td>
<td>41</td>
<td>59</td>
</tr>
</tbody>
</table>

Table 5 Results of the measurements of the radii of curvature of several locations on Fig. 31 using numerical method.

It is interesting to compare our results of ρc with those that can be obtained from the AFM images published by other researchers. From the interstep spacing data of Hsu et al. [28], we obtain a value of critical radius of 65Å (under the non-overlapping diffusion fields assumption) of MOCVD grown InP at growth temperature 600°C and reactor pressure 150 Torr. Our growth temperature is 540°C which is not much different from 600°C. The only difference is that our reactor pressure is 50 Torr instead of 150 Torr. According to the formula: ρc = γa/(kTσ), our ρc should be three
times larger under the reasonable assumption that our source gas partial pressure (proportional to \( \sigma \)) is roughly three times smaller. For the case of GaSb, there has been no report of spiral growth using MOCVD. However, Brar et al. observed MBE grown GaSb spirals whose morphology was very similar to ours. The only difference is that their spiral is much smaller than ours. From their interstep spacing data, we estimate a critical radius of about 20 \( \text{Å} \). This small value of \( c \) agreed with the argument [31] that MBE is a far from equilibrium process which should have a larger effective supersaturation.

4.4 Hollow core radius, specific surface free energy, and supersaturation.

The observation of hollow cores at the center of some multi-branch spirals and especially the observation of hollow core radius increasing with Burgers vector magnitude distinguishes our work from those of the others in this field. Other groups also observed well-resolved spirals growth in MOCVD or MBE grown III-V semiconductors [27-30] but none has observed hollow cores yet. In principle, parameters such as
the specific free energy and supersaturation can be obtained from hollow core radii. Historically, it was F.C. Frank [10] who first predicted that, for sufficiently large Burgers vectors, the screw dislocation should contain a observable hollow core whose radius is given by the so called Frank radius:

\[ r_0 = \frac{\mu b^2}{8\pi^2\gamma}, \]

where \( \mu \) is the shear modulus, \( b \) is the Burgers vector, and \( \gamma \) is the specific surface free energy (see section 2.2 of this thesis). Frank's prediction was qualitatively verified by the hollow cores observed in a lot of crystals. Hollow cores are often found at the center of growth spirals, as on silicon carbide (SiC) [37-40], copper indium sulfide, and pyrite [42]. Especially on SiC, spirals hollow cores are common (often with diameters 10 \( \mu \)m), which are caused by high Burgers vectors (often as high as 0.5 \( \mu \)m). As far as we know, all of the SiC spirals reported (with and without hollow cores) are one-branch (single) spirals and the magnitudes of their Burgers vector are equal to multiple monolayer step heights. For these spirals, the step heights are so large that a single branch spiral is sufficient to generate observable hollow cores. Recently multi-branch monatomic-height spirals with hollow cores were observed [43] in \( \text{KH}_2\text{PO}_4 \) (KDP) growth from solution. Such spirals are smaller compared with SiC spirals and need multi-branch steps to generate observable
hollow cores because the step height now is equal to one atomic height (several Å rather than the order of µm). Such spirals as well as hollow cores are so small that they are only observable under atomic force microscopy rather than phase contrast microscopy which was used to obtain SiC spiral images. Our group is the first one to observe such hollow cores in semiconductor growth of the commercially important III-V compounds. This observation should be useful for the understanding the MOCVD growth process.

Fig. 32 and Fig. 33 show the measurement of the hollow core radius $r_{hc}$ for a InAs 426 spiral with Burgers vector $b=4$ monolayer heights.
Figure 32 The measurement of the hollow core diameter on sample InAs 426 (n=4) along [110].
The hollow core radius for InAs 426 is estimated to be 30.3 nm by taking the geometric average value of the radii along the [110] and [110] directions. For GaSb (Sample: GaSb 714), the hollow core radius is
estimated to be 22.7 nm using similar measurement and data processing procedure (See Fig. 34 and Fig. 35)

Figure 34 The measurement of the hollow core diameter on sample GaSb 714 along [110].
Figure 35 The measurement of the hollow core diameter on sample GaSb 714 along [110].

Again we assume a non-overlapping diffusion fields (19ρc result). Recall equation (29) : \( r_{hc} = (1/2) \rho_c \left\{ (1+4r_0/\rho_c)^{1/2} -1 \right\} \), where \( \rho_c \) is the critical radius, \( r_0 \) is Frank radius which is equal to \( \mu b^2/(8\pi^2\gamma) \). The bulk modulus \( \mu \)
is equal to $1/2(c_{11} - c_{12})$ if we use an isotropic approximation for the shear stress [33]. $c_{11}$ and $c_{12}$ are the elastic moduli, defined by $X_i = \sum c_{ij} e_j$, where $X_i$ is the $i$th component of stress and $e_j$ is the $j$th component of strain. Table 6 shows tabulated values of $c_{11}$ and $c_{12}$.

<table>
<thead>
<tr>
<th></th>
<th>$c_{11}$ (in $10^{11}$ dyn cm$^{-2}$)</th>
<th>$c_{12}$ (in $10^{11}$ dyn cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InAs</td>
<td>8.329</td>
<td>4.526</td>
</tr>
<tr>
<td>GaSb</td>
<td>8.834</td>
<td>4.023</td>
</tr>
</tbody>
</table>

Table 6 Elastic moduli of InAs and GaSb [34].

The only unknown parameter in the equation is the specific surface free energy $\gamma$ which is numerically solved to be 4.6 mJ/m$^2$ for InAs and 5.7 mJ/m$^2$ for GaSb using equation (28). As a consistency check, we also measure the hollow core radii for other InAs spirals. Fig. 36 shows another hollow core observed at the center of a spiral with Burgers vector $\mathbf{b} = 6$ on sample InAs 426.
Another spiral \((n=6)\) with a hollow core at its center observed on sample InAs 426.

The shape of this hollow core is so irregular that the "measurement" of hollow core radius can only be treated as a rough estimate. The hollow core radius of this spiral is estimated to be 27 nm (see Fig. 37 and Fig. 38) and the corresponding specific surface free energy is calculated to be 12.3 mJ/m².
Figure 37 The measurement of the hollow core diameter on sample InAs 426 (n=6) along [110].
Figure 38 The measurement of the hollow core diameter on sample InAs 426 \( (n=6) \) along [110].

Fig. 39 shows the observation of a very large hollow core at the center of a spiral with Burgers vector \( n=12 \) on sample InAs 787.
The growth condition for InAs 787 is the same as that of InAs 426 except that InAs 787 epilayer thickness is 2.5 µm instead of 10 µm. We can thus safely assume that the critical radius of InAs 787 is the same as that of InAs 426 which is 19.5 nm although we do not have the data of far-from-
the-center interstep spacing for InAs 787. Fig. 40 and Fig. 41 show the measurements of the hollow core radius of InAs 787 in the [110] and [110] directions.

Figure 40 The measurement of the hollow core diameter on sample InAs 787 (n=12) along [110].
Figure 41 The measurement of the hollow core diameter on sample InAs 787(n=12) along [110].

The hollow core radius of InAs 787 is 88.7 nm after averaging the data from two directions. Keeping in mind our assumption about the critical
radius, the specific surface free energy of InAs is estimated to be 6.5 mJ/m² using the data from InAs 787.

Fig. 42 shows the observation of a hollow core at the center of sample InAs 1370 whose growth temperature is as low as 500°C.

Figure 42 A spiral (n=5) with a hollow core at its center. (sample InAs 1370)
The critical radius of InAs 1370 is calculated from far-away inter-step spacing measurement to be 17.7 nm. Fig. 43 and Fig. 44 show the measurement of the hollow core radius of the InAs 1370 spiral.

*Figure 43 The measurement of the hollow core diameter on sample InAs 1370 (n=5) along [110].*
Figure 44 The measurement of the hollow core diameter on sample InAs 1370 (n=5) along [110].

The hollow core radius of this spiral is measured to be 12 nm after averaging. The specific surface free energy is calculated to be 27.2 mJ/m²
after putting the data of critical radius and hollow core radius into that
equation. For all the hollow cores found, only two of them (InAs 426 (n=4)
and InAs 787 (n=12) ) are clear and measured without difficulties. In other
words, the growth parameters extracted from these two cores are more
reliable than those from the others.

It is interesting to compare the above estimates of \( \gamma \) with those
which can be found in the literature. We know that for Si, the values of \( \gamma \)
are 1500 mJ/m\(^2\) in vacuum, and 180-240 mJ/m\(^2\) in the presence of various
adsorbates. Our \( \gamma \) values are much smaller than these numbers, indicating a
quite different growth mechanism for MOCVD. On the other hand our
estimates of \( \gamma \) are much closer to the estimates for inorganic crystals grown
from solution, e.g. KH\(_2\)PO\(_4\) (24mJ/m\(^2\)) [35]. Since our growth is performed
under a large excess of adsorbed group V elements, the energy barrier for
the incorporation of group III elements should be much lower than vacuum
values of the surface energy. The existence of a liquid-like adsorption layer
has been postulated for many CVD systems [9].

Making use of equation (13) : 

\[
\rho_c = \gamma_o a / \{ kT \ln (\sigma + 1) \}
\]

where \( \sigma \) is the supersaturation of the vapor phase, \( a \) is the monolayer height and \( \gamma_o \) is
the energy of breaking one chemical bond. The relation between $\gamma_0$ and $\gamma$ should be that $\gamma_0 = \gamma \cdot a^2$. The values of supersaturation obtained by solving equation (13) are 0.058% for both InAs 426 and 0.053% for GaSb 714. The low value of supersaturation is consistent with the observation of pure spiral growth without any nucleation.

The results of the extraction of growth parameters using different spirals are summarized in Table 7. Because the growth rate is dominated by the supply of the Group III source, the supersaturation extracted should be related to the partial pressure of Group III source gas. The supersaturation and surface free energy have different values on the same sample (InAs 426) because we have two spirals with different Burgers vector and different hollow core radius on this sample. According to hollow core theory, all spirals should have a hollow core at their centers. In our experiments, spirals with Burgers vector $b=1$ or 2 have been observed. One possibility is that the resolution of our AFM (at most 15 nm lateral) is not good enough for such small hollow cores ($r_{hc}$ less than 15 nm for small Burgers vectors). Another possibility is that the hollow core theory which considers surface energy and strain only may have neglected other effects. We have no answer to this question are so far. Now we investigate the
relation between the magnitude of Burgers vector and the hollow core radius. The data we use are from InAs 426 (b=4) and InAs 787 (b=12) because only these two spirals give reliable measurements of hollow core radii. Theoretically, if we use Frank radius as a rough estimate of hollow core radius \( r_{hc} \), we have \( r_{hc} \sim b^2 \), and if we use the accurate formula: 

\[
r_{hc} = \frac{1}{2} \rho_c \left( \frac{1 + 4 r_0 / \rho_c}{1 + 4 r_0 / \rho_c} \right)^{1/2} - 1,
\]

we have \( r_{hc} \sim b^2 \) (when \( \rho_c \gg r_0 \)) and \( r_{hc} \sim b \) (when \( \rho_c \ll r_0 \)). Our experimental result for the critical radius shows \( \rho_c \sim r_0 \). Thus according to the theory, we should have roughly \( r_{hc} \sim b^{1.5} \). However, experimental result shows that \( r_{hc} \sim b \). This discrepancy may come from the uncertainty in the measurement of the hollow core radius because again we should be aware of the fact that the tip consists of hundreds of atoms. The discrepancy may also come from the fact that we have only two data points. Also the Burger vector \( b \) in InAs 787 may not be 12 because one or two branches in the spiral are not clearly ending with the dislocation center. If this is right, then we have \( b=11 \) or 10 and the discrepancy may be removed. It should be pointed out that these data were obtained using the assumption that the surface diffusion length is much smaller than the step spacing. On the other hand, if we use the overlapping diffusion fields result (\( x_c \gg \) inter-step spacing) we get much smaller
values of $p$, and even smaller values of $\gamma$ which do not seem physically reasonable. This is an indirect evidence that $x_s <<$ inter-step spacing.

\[
\text{Table 7 Growth parameter sets extracted from well-evolved spirals.}
\]

| Sample     | Group III gas partial pressure (Torr) | Temperature ($^\circ$C) | Burgers Vector (monolayers) | Critical Radius (nm) | Hollow-Core Radius (nm) | super-saturation of the Group III source gas (%) | surf.
energy (mJ/m$^2$) |
<table>
<thead>
<tr>
<th></th>
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<td>InAs426</td>
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<td>19.5</td>
<td>30</td>
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<td>4.5</td>
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<tr>
<td>InAs426</td>
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<td>540</td>
<td>6</td>
<td>n/a*</td>
<td>27</td>
<td>0.156</td>
<td>12.3</td>
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<tr>
<td>InAs787</td>
<td>0.0053</td>
<td>540</td>
<td>12</td>
<td>n/a**</td>
<td>89</td>
<td>0.082</td>
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<tr>
<td>InAs1370</td>
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<td>5</td>
<td>17.7</td>
<td>12</td>
<td>0.4</td>
<td>27.2</td>
</tr>
<tr>
<td>GaSb714</td>
<td>0.011</td>
<td>670</td>
<td>3</td>
<td>23.4</td>
<td>23</td>
<td>0.053</td>
<td>5.6</td>
</tr>
</tbody>
</table>

* and **: these two spirals do not have the data of far away inter-step spacing because the images were taken very near the center. In order to calculate surface energy, we assume that $p$, for these two spirals are equal to that of InAs426 ($b$=4), considering the growth conditions are the same for all these three spirals.

4.5 The applicability of BCF theory

We now discuss whether we can use BCF theory as a first order approximation to estimate the growth parameters of our MOCVD samples. Firstly, we point out the difference of vapor phase between these two cases. Fig. 45 (a) shows the case of BCF theory in which there is no carrier gas and the supersaturation is the same everywhere in the vapor phase. Fig.
45(b) shows the case of MOCVD in which there is a carrier gas in the vapor phase and the partial pressure of carrier gas is much much larger ($>10^4$) than that of the precursors.

**Figure 45 (a) and (b) Vapor phase difference between BCF picture and MOCVD.**

This will result in a steady diffusion of decomposed species through the boundary layer in which the hydrodynamic velocity of these species approaches zero. A steady concentration gradient of the decomposed species will formed in the boundary layer as these species are taken away on the crystal surface to growth sites. This situation is shown in Fig. 45(b) by the decreasing of point density when the interface is approached. Gilmer, Ghez, and Cabrera (GGC)[20] developed a crystal growth theory.
considering the effect of carrier gas. In this theory, two contributions to growth have been included. One is the diffusion from the crystal surface to kinks which is the main topic of BCF theory, the other is the diffusion through the vapor which is not considered in BCF theory. However GGC showed that when the mean free path (Λ) of the source gas in vapor phase is larger than its surface diffusion length (x_s), their theory came back to BCF theory. The condition Λ >> x_s is equivalent to stating that no gradients in the gas phase concentrations can exist on a length scale of order x_s. In other words, the gas phase supersaturation over the surface near a step edge must be roughly constant. BCF theory is based the assumption that there is no concentration gradient in the vapor phase at all in the plane of growth. So we can say the diffusion length in the vapor phase in BCF theory is infinitely large.

We now estimate the mean free path of group III elements in the vapor phase. We first consider InAs growth. As experimental evidence indicates that group III precursors decompose homogeneously, we consider the movement of In atoms rather than that of its organic compound. We consider only the collision between In atoms and hydrogen because of the
much higher partial pressure of hydrogen. From physical chemistry [21], the mean free path of an In atom is:

$$\Lambda = \frac{kT}{\pi(r_{\text{in}}+r_{\text{H}_2})^2p} \cdot \left\{ \frac{m_{\text{in}}+m_{\text{H}_2}}{m_{\text{H}_2}} \right\}^{1/2}$$

where $k$ is Boltzmann's constant, $T$ is the temperature, $r_{\text{in}}$ and $r_{\text{H}_2}$ are collision radii of In and hydrogen respectively, $p$ is equal to 50 Torr (the partial pressure of H$_2$), $m_{\text{in}}$ and $m_{\text{H}_2}$ are the masses of In and H$_2$ respectively. $r_{\text{in}}$ is found to be 1.6Å [22] and $r_{\text{H}_2}$ 2.72Å [23]. Putting all the data in the formula, $\Lambda$ is calculated to be 376nm. The mean free path of Ga in the growth of GaSb should be even larger because the GaSb growth temperature is 670°C and the atomic weight of Ga is less than that of In. For BCF theory to be applicable requires $x_s << 400$nm. We have no direct estimate of $x_s$ at present.

4.6 Temperature and morphology

We almost always grow InAs epilayers at a temperature of 540°C. This is from our experience based on a large amount of growths. We seem to have more chance to get morphologically very good samples at this
temperature. Morphologically good means being shiny to the naked eye, uniform and with low roughness from the point of view of AFM. However, morphologically good samples may be obtained when using other temperatures. For sample InAs 1370, we deliberately use a temperature as low as 500°C and find two interesting features with this sample. The first can be seen from Table 7 indicating that the supersaturation of this sample is higher than those of higher temperature samples. This may be explained by the fact that the equilibrium value of the vapor phase pressure will decrease with decreasing temperature. The actual pressure does not change at the lower temperature because it is set at 0.0053 Torr. Thus the supersaturation which is defined by the ratio of the actual pressure to the equilibrium pressure will increase with decreasing temperature. The second interesting feature seems related to the first. Fig. 46 shows typical concentric islands growth found on InAs 1370.
A hillock on InAs 1370 seems to have slightly more chance to be concentric steps than to be a spiral according to a large number of images of this sample. These concentric steps may come from another growth mechanism: the nucleation mechanism which dominates only at high supersaturation values. Although the supersaturation is relatively higher at...
500°C, the value is still too low to convince us that the conventional nucleation mechanism comes on stage. Conventional nucleation is a self-terminating process, i.e. when the top layer growth by nucleation finishes, new island has to be formed again on top of the surface. The formation of islands is difficult at low supersaturation values. So the explanation for the formation of these concentric islands is far from satisfactory. Nevertheless this observation indicates that MOCVD is very sensitive to the change of temperature as we have never seen such concentric islands at higher temperatures. Chernov [9] had another explanation for the concentric steps. Suppose initially, a circular step occurs on the surface. This step is a sink for adatoms and as time goes on, the radius of the circle will increase. A distribution of surface supersaturation forms on the circle with the minimum at the step edge and the maximum at the center. Chernov showed that the supersaturation at the center of the circle, i.e. the maximum one, increases with increasing radius. When the supersaturation at the center reaches the critical value, a second circular step will form on top of the first one. The process will repeat and result in the concentric steps. This kind of nucleation is called self-consistent nucleation and may explain the concentric steps on InAs 1370.
Fig. 47 shows the shapes of GaSb spirals at different temperatures.

![GaSb 751 Growth Temperature 560 °C](image1)
![GaSb 714 Growth Temperature 670 °C](image2)

Figure 47 GaSb spiral shapes under different growth temperature.

We can see that at lower temperatures, the "corners" become sharper and the "edges" become straighter and that at higher temperatures the rounding of the corners becomes considerable. The explanation of this temperature dependence can be found in section 15.1 in the original BCF paper [6]. The complete derivation is too lengthy to include in this thesis. We only present the result here. Fig. 48 shows a crystal nucleus with a "diameter" value of 1.
The radius of curvature $\rho$ of the nucleus at the corners is given by:

$$\frac{\rho}{l} = 2^{1/2}(kT/\phi)\tanh^2(\phi/2kT),$$

where $k$ is Boltzmann's constant, $T$ is temperature, $\phi$ is the nearest neighbors interaction. According to this expression, the nucleus would become a square at $T = 0$ K ($\rho=0$) and become more and more like a circle ($\rho \approx l/2$) with $T$ increasing at the growth temperature range.
4.7 Anisotropy

All of our pictures of InAs or GaSb show an anisotropic effect, i.e. the overall shape of the spirals or closed loops is elliptical (InAs) or rectangular (GaSb) rather than circular or square. Our RDS (reflectance difference spectroscopy) experiment shows that the InAs spiral ellipse elongates along the [110] direction. The III-V bonding structure of a [110] step is much different from that of a [110] step. Fig. 51 makes it clear what we mean by [110] and [110]. Such conventions about the choices [110] and [110] are widely used in the research of III-V semiconductors. We can easily find the ratio of the [110] growth velocity to the [110] growth velocity by measuring the step spacing along the direction of the axes'. An alternative and maybe more accurate method is to measure the lengths of major and minor axes. Fig. 49 shows the results of our measurement of anisotropy on the InAs [001] surface. The ratio of the major axis length to the minor axis length is equal to the ratio of the
growth velocity along the corresponding direction. This ratio is estimated to be 1.4 after averaging data from two ellipses measured.

\[
\text{major axis length} = 1.89 \text{ micron} \quad \text{minor axis length} = 1.39 \text{ micron}
\]

\[
\text{major axis length} = 2.60 \text{ micron} \quad \text{minor axis length} = 1.74 \text{ micron}
\]

*Figure 49 Measurements of the anisotropy of growth velocity on InAs.*

Fig. 50 shows the measurements concerning GaSb anisotropic effect. Several experimental works have reported on the spiral growth of
GaSb using MBE [26] [27]. Although we don't know the orientation of the spirals shown in Fig. 50, by comparison with these works, we conclude that the major axis is lined up along [110].

Figure 50 Measurements of the anisotropy of growth velocity on GaSb.
These measurements show that the anisotropic factor of GaSb is almost 2 which agrees with the experimental results of Brar et al. [26] The spiral is generally elongated in the [110] direction. Fig. 51 shows the explanation of GaSb anisotropy. Because the growth rate is dominated by the movement of the Group III element, the attachment of the Ga is our main concern. Brown et al. [27] observed that GaSb spirals elongate along [110] at the temperature of 400°C and elongate along [110] when the temperature is higher than 475°C. The following argument can explain the transition. The attachment of a Ga atom at the [110] step forms three bonds, whereas the attachment of a Ga atom at the [110] step forms only two bonds. In other words, the [110] attachment is more energy favorable and the growth along [110] should be faster. This is true at lower temperatures when the desorption of Sb atoms is not a problem. At higher temperatures, the desorption of a Sb atom in the [110] step is much easier because it has only one bond with a Ga atom in the crystal. In the case the [110] step, the corresponding number of bonds is two and the desorption is more difficult. Thus the anisotropy of GaSb spirals is explained if we consider the attachment of Ga atoms and the desorption of As atoms at the
same time. The growth temperature of our GaSb sample is as high as 670°C, the spirals should elongate along $[1\bar{1}0]$ according to the theory above. Similar arguments may also explain the anisotropy of the spirals on InAs samples which are grown at 540°C.

![Diagram of bonding structure](image)

Figure 51 The bonding structure of $[110]$ and $[\bar{1}10]$ steps [51].
Chapter 5. Summary and Conclusions

AFM is a useful tool for obtaining the value of dislocation densities in relaxed epitaxial layers, which is a crucial factor to semiconductor growth and device fabrication. The dislocation density's dependence on substrate materials (lattice mismatch), temperatures, and epilayer thickness can be investigated by data from large scale AFM images. The magnitude of strain as well as other factors determines the dislocation density. Suitable strength of strain seems to be important if one wants to obtain well-resolved spirals.

For the first time, especially for the first time in case of MOCVD growth technique, important physical parameters such as the critical radius, surface diffusion length, surface evaporation energy, specific surface free energy, supersaturation are estimated quantitatively from the measurements on AFM images of well-resolved spirals. The very small value of specific surface free energy implies MOCVD growth is quite different from the growth from melt and more like the growth from solution. However these data represent preliminary estimates of surface energy, a difficult parameter to obtain experimentally. Further work will be
required to verify that these hollow cores are not due to non-equilibrium effects such as etching during cool down.

The mean free path for gas phase diffusion appears to be larger than but certainly not smaller than the surface diffusion length of adatoms. BCF theory is likely a very useful starting point in the analysis of spiral morphology of MOCVD-grown III-V semiconductors. Further analytical methods, such as direct measurement of the surface adatom concentration would be useful as a check on the growth parameter estimates obtained in this work.
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APPENDIX

The ideal gas equation for the vapor phase reads:

\[ P = nkT \]  \hspace{1cm} (1)

where \( P \) is the pressure, \( n \) the molecule number density, \( k \) the Boltzmann's constant, and \( T \) the temperature.

The flux \( j_v \), which is equal to the number of molecules from the vapor to the crystal surface per unit time per unit surface area is \((1/4)nV_{\text{avg}}\), where \( V_{\text{avg}} \) is the average velocity of gas molecules which is equal to \( \{8kT/(\pi m)\}^{1/2} \).

(The derivation of these two formulas can be found in many books about ideal gas). Using these two formulas and (1), we can derive equation (2):

\[ j_v = P/(2\pi mkT)^{1/2} \]  \hspace{1cm} (2)

The flux \( j_v \), which is equal to the number of the desorbed molecules from the crystal surface into the vapor per unit time per unit area is \( n_s/\tau_s \), where \( n_s \) is the adsorbed molecule number density, and \( \tau_s \) the average life time of an adsorbed molecule on the surface. In equilibrium, \( j_v \) is equal to \( j_v \), thus we have equation (3):

\[ P_0/(2\pi mkT)^{1/2} = n_s/\tau_s \]  \hspace{1cm} (3)
where $P_0$ is the equilibrium pressure, and $n_{s0}$ the equilibrium adsorbed molecule number density. In the case of growth, the actual pressure $P$ is $\alpha P_0$, and the actual adsorbed molecule number density $n_s$ is $\alpha_s n_{s0}$, where $\alpha$ and $\alpha_s$ are saturation ratios of the vapor and surface respectively. Now $j_{vc}$ is no longer equal to $j_{cv}$ and there is a net flux $j_v$ from the vapor to the surface which results in growth. So $j_v$ should be equal to $j_{vc}$ minus $j_{cv}$:

$$j_v = P/(2\pi mkT)^{1/2} - n_s/\tau_s = \alpha P_0/(2\pi mkT)^{1/2} - \alpha_s n_{s0}/\tau_s$$

Using equation (3) $j_v$ can be simplified as:

$$j_v = (\alpha - \alpha_s) n_{s0}/\tau_s$$

The above equation is equation (9) in the main text.