Towards the Development of InAs/GaInSb
Strained-Layer Superlattices for Infrared Detection

by

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Dedicated to my parents

‘Nearly all the atoms in your body were once cooked in the nuclear furnace of an ancient supernova – you are truly made of stardust.’

Francis Collins (Director of the Human Genome Project)
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**Summary**

This study focuses on the development of InAs/GaInSb strained-layer superlattice structures by metal organic chemical vapour deposition (MOCVD), and deals with two aspects of the development of InAs/GaInSb SLS’s by MOCVD viz. the deposition of nano-scale (~100 Å) GaInSb layers, and the electrical characterization of unstrained InAs.

The first part of this work aims to study the MOCVD growth of GaInSb layers in terms of deposition rate and indium incorporation on the nano-scale. This task is approached by first optimizing the growth of relatively thick (~2 µm) epitaxial films, and then assuming similar growth parameters during nano-scale deposition. The GaInSb layers were grown as part of GaInSb/GaSb quantum well (QW) structures. By using this approach, the GaInSb QW’s (~100 Å) could be characterized with the use of photoluminescence spectroscopy, which, when used in conjunction with transmission electron microscopy and/or X-ray diffractometry, proves useful in the analysis of such small scale deposition. It is shown that the growth rate of GaInSb on the nano-scale approaches the nominal growth rates determined from thick (~2 µm) GaInSb calibration layers. The In incorporation efficiency in nano-layers, however, was markedly lower than what was predicted by the GaInSb calibration layers. This reduction in indium incorporation could be the result of the effects of strain on In incorporation. The choice of substrate orientation for QW deposition was also studied. QW structures were grown simultaneously on both (100) and 2°off (100) GaSb(Te) substrates, and it is shown that growth on non-vicinal substrates is more conducive to the deposition of high quality QW structures.

The second part of this study focuses on the electrical characterization of unstrained InAs. It is long known that conventional Hall measurements cannot be used to accurately characterize InAs epitaxial layers, as a result of parallel conduction resulting from surface and/or interface effects. This study looks at extracting the surface and bulk electrical properties of n-type InAs thin films directly from variable magnetic field Hall
measurements. For p-type InAs, the situation is complicated by the relatively large electron to hole mobility ratio of InAs which tends to conceal the p-type nature of InAs thin films from Hall measurements. Here, this effect is illustrated by way of theoretical simulation of Hall data.
Chapter 1: Introduction

The development of infrared (IR) detection devices is largely driven by military endeavors. The present emergence of third generation IR detectors aims to improve the detection and identification of military targets by developing multi-spectral IR detection technology (Rogalski and Martyniul, 2006). As shown in Figure 1.1, every target has a unique IR ‘fingerprint’ (FAS, 2007) consisting of both mid-wavelength IR (MWIR) and long-wavelength IR (LWIR) components. The advantage of multi-spectral IR focal plane arrays (FPA’s) over single wavelength detection devices is that such detectors use both MWIR and LWIR radiation to better discriminate the unique signatures of objects in a scene, and can thus be used to better distinguish between missile targets, warheads, and decoys. Multi-spectral IR FPA’s are also used in civilian applications such as Earth and planetary remote sensing, and astronomy (Rogalski and Martyniul, 2006).

Figure 1.1: Infrared signatures of military targets (FAS, 2007).

At present, AlGaAs/GaAs quantum-well infrared photodetectors (QWIP’s) and HgCdTe (MCT) infrared detectors are the dominant technologies for MWIR (3 -5 µm) and LWIR
(8 - 14 µm) FPA applications (Smith and Mailhiot, 1987; Grein et. al., 1995; Kim and Li, 2003; Rogalski and Martyniul, 2006). Despite considerable progress in MCT technology, difficulties still remain. In particular, for wavelengths exceeding 10 µm (Smith and Mailhiot, 1987), device performance is limited by large tunneling dark currents which lower the detectivity of devices, as well as high Auger recombination rates which lower quantum efficiency. In addition, the energy gap of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ is very sensitive to composition control. For example, at 77 K, a variation of $\Delta x = 0.2\%$ gives a variation in the device cut-off wavelength of $\Delta \lambda_c = 0.064\,\mu m$ at $\lambda_c = 5\,\mu m$, but $\Delta \lambda_c = 0.51\,\mu m$ at $\lambda_c = 14\,\mu m$ (Rogalski and Martyniul, 2006). Thus the required composition control is much more stringent for LWIR than for MWIR MCT devices. Regarding QWIP’s, there is difficulty in achieving high device performance at higher temperatures due to the inherent short carrier lifetimes and high thermal generation rates which, respectively, limit the quantum efficiency and operating temperature.

An attractive alternative to bulk MCT and QWIP’s is the InAs/GaInSb strained-layer superlattice (SLS) which may be advantageous over these technologies in applications requiring higher operating temperatures or longer wavelength detection. Detectors using these SLS’s are expected to have quantum efficiencies that are comparable with those of MCT, yet lower dark currents due to a larger electron effective mass (Rogalski and Martyniul, 2006) and enhanced lifetimes due to slower Auger recombination rates (Grein et. al., 1995). In addition, bandgaps are subject to the control of the superlattice (SL) layer thickness rather than composition, resulting in an improved uniformity across the wafer.

The successful epitaxial growth of InAs/GaInSb SLS structures is well documented (Zborowski et. al., 1992; Van Hove et. al., 1994; Brown et. al., 1997; Lin et. al., 2000), and for a review on the development of InAs/GaInSb SLS’s, the reader is referred to literature (Young et. al., 1998; Johnson, 2000; Brown, 2005; Rogalski, 2005). So far, the deposition of InAs/GaInSb SLS’s has been mainly achieved by molecular beam epitaxy (MBE). This study focuses on the growth of InAs/GaInSb SLS structures by metal organic chemical vapour deposition (MOCVD), and deals with two aspects of the
development of InAs/GaInSb SLS’s by MOCVD viz. the deposition of nano-scale (~100 Å) GaInSb layers, and the electrical characterization of unstrained InAs.

The development of InAs/GaInSb SLS structures requires the reproducible two-dimensional growth of uniform InAs and GaInSb epitaxial layers. Since the average thickness of constituent SLS layers is of the order of 50 Å and 20 Å for InAs and GaInSb layers, respectively (Kim and Li, 2003), low deposition rates (< 10 Å/s) are required. The first part of this work aims to study the MOCVD growth of GaInSb layers in terms of deposition rate, growth mode, and indium incorporation on the nano-scale. For reasons discussed in the text (introduction to Chapter 6), the nano-scale deposition of InAs was not considered in this study.

The second part of this study focuses on the electrical characterization of unstrained InAs. Hall measurements carried out on thick (~ 2 µm) calibration layers is generally used to predict the electrical properties of strained layers in SLS devices. It is long known, however, that conventional Hall measurements cannot be used to accurately characterize InAs epitaxial layers, as a result of parallel conduction resulting from surface (Wieder, 1974; Noguchi et. al., 1991; Wang et. al., 1992; Olsson et. al., 1996; Piper et. al., 2006) and/or interface effects (Yamaguchi et. al., 1998; Wolkenberg et. al., 2000; Cai et. al., 2004; Okamoto et. al., 2005). Knowledge of the true electrical properties of InAs is essential in the design of SLS devices. This study looks at extracting the surface and bulk electrical properties of n-type InAs thin films directly from variable magnetic field Hall measurements (Botha et. al., 2005; Krug et. al., 2007). For p-type InAs, the situation is complicated by the relatively large electron to hole mobility ratio of InAs which tends to conceal the p-type nature of InAs thin films from Hall measurements. Here, this effect is illustrated by way of theoretical simulation of Hall data (Botha, Shamba and Botha, 2008).

The outline of this dissertation is as follows: In Chapter 2 a brief account of InAs/GaInSb SLS structures is given, with a focus on band alignment and SLS design. The MOCVD process is discussed in Chapter 3, and Chapter 4 contains a summary of the
characterization techniques used in this study. Chapters 5 and 6 are the results chapters, and deal with the development of GaInSb nano-layers, and the electrical characterization of bulk InAs, respectively. The study is concluded in Chapter 7.
Chapter 2: InAs/GaInSb Superlattices

In this chapter, InAs/GaInSb SLS’s are briefly discussed in terms of band alignment and SLS design.

2.1. Band Alignment

The concept of a SL was first introduced in 1970 by Esaki and Tsu (Esaki and Tsu, 1970). They postulated that a semiconductor heterostructure having a one-dimensional periodic variation in alloy composition or dopant concentration (referred to as a superlattice) would exhibit intriguing transport properties as a result of quantum-mechanical effects. Subsequent to their proposition, molecular beam epitaxy was developed, which allowed for the deposition of such fine heterostructures (constituent layers ~ 10 to 100 Å thick). Then, in 1977, Sai-Halasz, Tsu, and Esaki (Sai-Halasz, Tsu and Esaki, 1977) further proposed the idea of what is now known as a type-II superlattice. An example of such a structure is the InAs/GaInSb SLS, in which the conduction band minimum (CB) of InAs is below the valence band maximum (VB) of

![Figure 2.1: Band alignment of the InAs/Ga$_{1-x}$In$_x$Sb strained-layer superlattice (Rogalski and Martyniul, 2006).]
GaInSb. The band alignment of an InAs/GaInSb SLS is given in Figure 2.1. For reference purposes, the unstrained band alignment of InAs, GaSb and InSb is shown to scale in Figure 2.2. Here, energy bands have been drawn with respect to the valence band of unstrained InSb. With the type-II band alignment, a superlattice can have a bandgap that is smaller than that of either constituent material. The internal strain resulting from the lattice mismatch between InAs and GaInSb lowers the conduction band minimum of InAs and raises the heavy-hole band in GaInSb by the deformation potential effect. This, together with the effects of quantum confinement, creates a situation in which the energy bandgap of the superlattice can be adjusted to form either a semimetal (for thick InAs and GaInSb layers) or a narrow bandgap (for thinner, < 50 Å, layers) semiconductor material (Rogalski and Martyniul, 2006).

In the InAs/GaInSb SLS structure, the type-II band alignment results in the spatial separation of holes and electrons, and holes tend to localize in the GaInSb layers, while electrons tend to localize in the InAs layers. The bandgap of the SLS is determined by the energy difference between the first electron state E1 in the InAs layers and the first heavy hole state HH1 in the GaInSb layers, and can be varied continuously in a range between 0 and about 250 meV (Rogalski and Martyniul, 2006). A more comprehensive discussion on the effects of lattice strain and quantum confinement is given in subsequent sections (see sections 5.1 and 5.2).

Since the electrons and holes are spatially separated, the optical matrix elements decrease rapidly with increasing layer thickness. As already mentioned, the misfit strain between InAs and GaInSb lowers the conduction band minimum of InAs and raises the heavy-hole band in GaInSb. Thus, for a given SL layer thickness, the SL bandgap is lowered by an increase in indium content. In the case of the InAs/GaSb SL, originally proposed by Sai-Halahasz, Esaki and Harrison (Sai-Halasz, Esaki and Harrison, 1978), the SL bandgap depends only on SL layer thickness and the effects of quantum confinement, and low bandgaps are only achieved with relatively thick SL layer thicknesses. Therefore, the optical matrix elements of this structure are small. It follows that the absorption
The first suggestion of the InAs/ GaInSb SLS for IR detection was given by Smith and Mailhiot in 1987 (Smith and Mailhiot, 1987). For a given SL layer thickness, the bandgap of the SL can be reduced by increasing the InSb content in the GaInSb layers. Thus, small
bandgap SL’s can be obtained with sufficiently thin SL layers to maintain absorption coefficients on par with that of MCT.

Furthermore, the Auger recombination rate in InAs/GaInSb SLS’s can be suppressed by the valence band splitting caused by lattice mismatch in p-type structures for LWIR detection (Grein et. al., 1995). The influence of HH-LH splitting on Auger recombination for a p-type InAs/GaInSb SLS is illustrated in Figure 2.3 (Grein et. al., 1995). In the figure, the Auger recombination transitions of bulk MCT (a), a MWIR InAs/GaInSb SL (c), and a LWIR InAs/GaInSb SLS (b) are compared. For the LWIR SLS the p-type Auger recombination is suppressed due to one of the holes being forced into a region of low occupation by energy and crystal momentum conservation. For the MWIR SL however, the p-type Auger recombination is more pronounced because the bands permit recombination transitions to occur with both holes in regions of relatively high occupation (Grein et. al., 1995). Thus, the probability, and hence the rate, of Auger recombination is greatly reduced for LWIR SLS’s. On the contrary, MWIR SL’s show no advantage over MCT in terms of Auger recombination suppression, and it can be concluded that InAs/GaInSb SLS’s are only advantageous over MCT in the LWIR region.

Figure 2.3: Comparison of p-type Auger recombination transitions in bulk MCT and InAs/GaInSb superlattices. (Grein et. al., 1995).
2.2. Lattice Matching

For a SLS structure to be free from misfit dislocations two main criteria need to be met. Firstly, the constituent layers of the SLS have to be thinner than their individual critical thickness limitations (Critical layer thickness and misfit dislocations in heterostructures are discussed in section 5.1.1). Secondly, the average lattice parameter of the SLS has to match that of the substrate or buffer layer onto which the structure is deposited i.e. the tension and compression experienced by the constituent layers in the SLS has to be balanced. If this is not the case, then misfit dislocations will be introduced at the interface between the SLS and the substrate (or buffer layer) when the SLS is above a certain critical thickness. In Figure 2.4 the tension and compression experienced by InAs and GaInSb layers, respectively, in the interface planes of InAs/GaInSb SLS’s is illustrated.

![Figure 2.4: Illustration of tension and compression experienced by InAs and GaInSb layers, respectively, in the interface planes of InAs/GaInSb SLS’s.](image)

2.3. Superlattice Design

In addition to the capability of adjusting the band gap energy, InAs/GaInSb SLS’s have the added capability of energy band structure engineering, since the same bandgap energy
can be designed using different combinations of layer thickness and composition. By examining the band structure of designs, equivalent in terms of peak wavelength sensitivity, the optimum design can be selected to enhance parameters such as infrared absorption coefficient, electron effective mass, and charge carrier lifetime (Kim and Li, 2003).

A theoretical investigation of InAs/GaInSb SLS’s for LWIR detection has been carried out by Kim and Li (Kim and Li, 2003). By considering critical layer thickness limitations (section 5.1.1), they designed InAs/GaInSb SLS’s for LWIR applications with the aim of maximizing the absorption coefficient of structures, while minimizing Auger recombination rates.

The optical matrix elements, and hence the absorption coefficient, of SLS’s is maximized by minimizing the thickness of constituent layers. Due to the effects of quantum confinement, a decrease in the SLS layer thickness will be accompanied by an increase in the SLS bandgap. This increase in SLS bandgap is undesirable for LWIR applications, and, for a given detection wavelength, a decrease in SLS layer thickness must be accompanied by an increase in the In content of the GaInSb layers (the misfit strain between InAs and GaInSb lowers the conduction band minimum of InAs and raises the heavy-hole band in GaInSb and hence lowers the bandgap of a SLS).

The effect of InSb content on valence band splitting in InAs/GaInSb SLS structures was calculated by Kim and Li for various device wavelengths, and their results are illustrated in Figure 2.5. In the figure, $\Delta E_{hh}$ denotes the change in HH-LH splitting. The Auger recombination rate can be minimized by increasing the extent of HH-LH splitting in the GaInSb layers. This is achieved by increasing the In content in the GaInSb layers (Figure 2.5). A decrease in SLS bandgap is also achieved by increasing the InSb content in the GaInSb layers. It thus follows, that for a given bandgap, both the SL layer thickness and the Auger recombination rate can be minimized by increasing the InSb content in SLS structures. Kim and Li found that by increasing the InSb content in the GaInSb layers, while maintaining a balance between the compression and tension in a SL structure, the
valence band splitting increases only to a point, after which either no further increase in valence band splitting is observed, or a decrease in valence band splitting is expected for higher In concentrations (Figure 2.5). The higher the InSb content, the lower the critical layer thickness (section 5.1.1), and thus the optimum InSb concentration has an upper limit, above which misfit dislocations become more prevalent. For this reason, only InSb concentrations of less than 30 % are considered in the design of LWIR SLS’s (Figure 2.5).

![Figure 2.5: Change in valence band splitting versus In content in GaInSb. Each data point denotes theoretical calculations. The balance between tension and compression in the superlattice was maintained in calculations. (Kim and Li, 2003)](image)

The SLS designs of Kim and Li range from 38.7 Å/15.5 Å InAs/Ga$_{0.75}$In$_{0.25}$Sb layers for 9.08 µm IR detectors, to 51.2 Å/17.2 Å InAs/Ga$_{0.70}$In$_{0.30}$Sb layers for 18.91 µm LWIR detection devices. Thus, layer thicknesses of ~ 50 Å and ~ 20 Å are required for the InAs and GaInSb components, respectively, of a LWIR detector. It follows that fairly low deposition rates (in order to achieve such thin layers) and a moderately high In content is required in the deposition of LWIR InAs/GaInSb SLS’s.
Chapter 3: Metal Organic Chemical Vapour Deposition

The fundamental aspects of Metal Organic Chemical Vapour Deposition (MOCVD) have been discussed by Stringfellow in his book entitled ‘Organometallic Vapour-Phase Epitaxy: Theory and Practice’ (Stringfellow, 1989). Along with many additional contributions, a more recent review article on the topic has been provided by the same author (Stringfellow, 2001). The information presented in this chapter is based on these references.

Simply put, the deposition of epitaxial thin films is achieved via the pyrolysis of a dilute gaseous mixture of precursors and the subsequent recombination of atomic species on a heated (see section 3.1.3) substrate. The supersaturation of the input vapour relative to the solid is the driving force of the growth process.

This study involves the MOCVD growth of the III/V semiconductor binaries InAs and GaSb, and the ternary GaInSb. In this chapter, the basic growth parameters are discussed, and a description of the growth system used in this study is given.

3.1. Fundamentals

3.1.1. Mole Fraction

The mole fraction (MF) of a given precursor is defined as

\[ MF = \frac{n_{\text{precursor}}}{n_{H_2}} \]  \hspace{1cm} (3.1)

where \( n_{\text{precursor}} \) is the precursor flow rate (mol/min) through the reactor, and \( n_{H_2} \) is the
hydrogen flow rate (mol/min) through the reactor. Here, hydrogen is used as a carrier gas, transporting the reagents from the input manifold to the reaction interface (section 3.2) at a rate of 2.15 liters/min. The comparison of precursor mole fractions gives an indication of the relative concentrations of precursors in the reactor.

3.1.2. V/III Ratio

The MOCVD growth of III/V semiconductors is usually carried out under group V rich conditions. That is, the molar ratio of the group V atoms to the group III atoms is greater than unity. The reason for this is that the group V elements typically have high vapour pressures at normal growth temperatures, and excess group V atoms can escape to preserve the desired stoichiometry of the solid. The group III elements, however, are less volatile, and tend to form secondary phases when in excess. The latter is true for the MOCVD growth of InAs. Since arsenic has a high vapour pressure, the V/III ratio for InAs does not have to be precisely controlled. In the case of antimony-based semiconductors, however, the V/III ratio at the growth interface has to be as close to unity as possible (Biefeld, 2002). This is because Sb has a low vapour pressure and tends to form secondary phases on the growth surface if present in excess. Thus the V/III ratio at the growth interface of GaSb and GaInSb is limited to being close to unity, since both the group III and the group V components will produce secondary phases when present in excess.

Since the V/III ratio in the vapour phase is limited to being greater than or equal to unity, the group III species becomes the growth rate limiting species in the deposition of III/V semiconductors, since all the group III atoms reaching the growth interface will be incorporated. If follows, that the total MF of the group III precursors can be varied to control the growth rate of a particular layer.

The concentration of native defects (vacancies, interstitials, and antisites) and the incorporation of dopants depend on the stoichiometry (atomic composition) of the solid,
which in turn depends on the growth temperature and the V/III ratio at the vapour/solid interface. Here, a distinction is made between the input molar V/III ratio of precursors and the V/III ratio at the growth interface, since the latter depends on the pyrolysis (decomposition) efficiency of the precursors. If one or more of the precursors are not completely pyrolysed at the chosen growth temperature, then the atomic V/III ratio can differ from the precursor V/III ratio.

When discussing growth parameters, the V/III ratio referred to is the input molar ratio of the precursors. The V/III ratio is varied at a given temperature to optimize the solid stoichiometry.

### 3.1.3. Precursor Chemistry

The activation energy required for the pyrolysis of an organometallic precursor is defined by the dissociation energy required to break the first metal-carbon bond of a precursor molecule. This dissociation energy is listed in Table 3.1 for TMGa, TMIn, and TMSb. It is seen that the TMIn molecule requires less dissociation energy than both TMGa and TMSb, and is thus expected to dissociate at a lower ambient temperature than the TMGa and TMSb molecules. According to Graham et. al. (Graham et. al., 1993), both TMGa and TMSb are roughly 50% dissociated at 560 °C, while TMIn shows complete pyrolysis at 550 °C. Thus, as the growth temperature is increased above 550 °C the concentration of Ga an Sb in the vapour will increase until both precursors are fully pyrolysed, while the concentration of indium in the vapour will remain the same.

### 3.1.4. Vapour-Phase Composition

In the deposition of the Ga$_{1-x}$In$_x$Sb alloy, mixing occurs on the group III sublattice. The vapour phase composition ($x_v$) of the group III precursors is defined as
where \( n_{TMIn} \) and \( n_{TMGa} \) are the molar flow rates of the group III precursors.

The solid composition of the ternary is limited by the mass transport of the group III elements to the growth interface and is given by

\[
x = \frac{r_{g, InSb}}{r_{g, InSb} + r_{g, GaSb}}
\]

where \( r_g \) is the growth rate of the binary compound. The enthalpies of formation of GaSb and InSb are in the regions 9.4-11 and 6.8-10 kcal/mol, respectively. Thus, the growth of GaSb is thermodynamically favoured over the growth of InSb. For mass transport limited MOCVD i.e. when the atomic V/III ratio is greater than unity, the binary growth rate is linearly proportional to the MF of the limiting species. As the growth temperature is increased in the temperature region where TMGa and TMSb are not yet fully pyrolysed, the composition of Ga and Sb in the vapour increases, while the concentration of indium in the vapour remains the same. Thus, as the growth temperature is increased, \( r_{g, GaSb} \) increases, while \( r_{g, InSb} \) remains unchanged. This increase in GaSb growth rate leads to a decrease in the incorporation of indium in the solid. In addition, the increase in pyrolysed TMGa leads to an increase in the total group III MF, and the overall growth rate of the solid increases.

The distribution coefficient \((k)\) is defined as the ratio

\[
k = \frac{x}{x_v}
\]

For higher growth temperatures, where all the precursors are completely pyrolysed, the distribution coefficient approaches unity. However, as the growth temperature drops, the
atomic concentration of Ga in the vapour decreases, and the distribution coefficient exceeds unity.

At low V/III ratios (atomic V/III ratio < unity) not all of the group III species can be incorporated into the solid, and the Ga and In atoms compete to occupy the group III sublattice. Thus there is a decrease in the incorporation of In as the atomic V/III is reduced below unity since the deposition of GaSb is thermodynamically favoured.

3.2. The Growth System

In this work, growth was carried out at atmospheric pressure, using a Thomas Swan Epitor 04 research scale MOCVD reactor. A detailed schematic of the system is shown in Figure 3.1.

3.2.1. General Description

As already mentioned, the deposition of epitaxial thin films is achieved via the pyrolysis of a gaseous mixture of precursors and the subsequent recombination of atomic species on a heated substrate. In this work, the substrate is placed on a molybdenum susceptor, inside a quartz reactor tube. The susceptor is heated by a quartz tungsten halogen lamp, and the growth temperature is maintained by a Eurotherm 2604 temperature controller. Reagents enter the reactor from the input manifold and, after passing through the reactor, are expelled through the exhaust system.

3.2.2. Precursors

This study deals with the deposition of GaSb, GaInSb, and InAs (undoped and Zn-doped) epitaxial layers. The precursors used in this study are listed in Table 3.1. TMGa, solution TMIn, TMSb, and TBAs are all liquid sources, and are contained in stainless steel
bubblers. The DMZn source is a gas mixture of hydrogen and DMZn with a concentration of 200 ppm DMZn.

The liquid and vapour phases of the source material within a bubbler coexist in equilibrium. Each bubbler is maintained in a constant temperature bath, and the relationship between the bath temperature (T) and the vapour pressure (P) in a bubbler is given below, where A and B are the gas constants of a given source.

\[
\log P(\text{torr}) = B - \frac{A}{T(K)} \tag{3.5}
\]

The bath temperature and gas constants of the respective precursors are listed in Table 3.1.

In order to transport vapour from a liquid source, a carrier gas is sent through the bubbler. In this way, vapour of the source mixes with the carrier gas and is carried away to the input manifold. The molar rate (n) of source material picked up by the carrier gas as it moves through a bubbler is obtained from the ideal gas law, and is given by

\[
n = \frac{PV}{RT} = FV \tag{3.6}
\]

where V is the volumetric flow rate of the carrier gas through the bubbler, and R is the universal gas constant.

In the case of the DMZn gas mixture no carrier gas is required and the relationship between the molar (n) and the volumetric (V) flow rates of DMZn towards the input manifold is given by

\[
n = \frac{m}{M_R} = \frac{\rho V}{M_R} = FV \tag{3.7}
\]
where \( m \) is the mass, \( M_R \) the molar mass, and \( \rho \) the density of DMZn. Since the DMZn gas mixture contains only 200 ppm DMZn, the factor \( F \) becomes

\[
F = \left( \frac{200}{1 \times 10^6} \right) \left( \frac{\rho_{\text{DMZn}}}{M_R} \right)
\]

Similarly, the molar flow rate of hydrogen flowing through the reactor from the main carrier line can be obtained from Equation 3.7.

The density and molar mass of DMZn and \( \text{H}_2 \) are given in Table 3.1 together with the factor \( F \) for all precursors used in this study.

### 3.2.3. The Gas System

Palladium diffused hydrogen is used as a carrier gas and feeds Manifolds A and B. Manifold A feeds a mass flow controller on each bubbler line, which feeds a four-way valve. At this point, the carrier gas is either directed through the bubbler or the bubbler is bypassed and only hydrogen is sent to the input manifold. Similarly, Manifold B feeds the DMZn source line with hydrogen. A three-way valve is used to switch between feeding the mass flow controller on this line with either hydrogen or the DMZn gas mixture. At the input manifold, each reagent is met by another three-way valve, and is either diverted to the vent manifold and swept to waste with the vent gas, or the reagent is diverted into the carrier gas line.

The carrier and the vent flows are controlled by mass flow controllers fed by Manifold B, and the carrier gas is connected to the core of the input manifold, passing close to the valve seat of each reagent line and on to the reactor. Thus the reagent gasses can be rapidly diverted into the carrier gas stream. Due to the proximity of the valve seat to the carrier gas (~0.02 cc), there is no gradual reduction in reagent as the reagent is switched out of the reactor, thus allowing for the deposition of abrupt interfaces.
Figure 3.1: Schematic of the Metal-Organic Chemical Vapour Deposition System used in this study.
<table>
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<th>Precursor</th>
<th>Chemical Symbol</th>
<th>$\rho$ (g/cc)</th>
<th>$M_R$ (g/mol)</th>
<th>Gas constants</th>
<th>Bath temp (°C)</th>
<th>$F$ (mol/cc)</th>
<th>Bond strength (kcal/mol)</th>
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<tr>
<td>hydrogen</td>
<td>H$_2$</td>
<td>8.97×10$^{-5}$</td>
<td>2.016</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.45×10$^{-5}$</td>
</tr>
</tbody>
</table>
Chapter 4: Characterization Techniques

In this chapter the various characterization techniques employed in this study are briefly discussed.

**4.1. Hall Measurements**

The standard van der Pauw technique (Van der Pauw, 1958) was used to carry out Hall measurements in this study. In order to prepare samples for Hall measurements, four indium dots were soldered onto the four corners of a sample ~ 6x6 mm in size. The sample was then annealed at 350 °C for 5 minutes in flowing nitrogen to form good ohmic contacts.

For the variable temperature and variable magnetic field Hall measurements, samples were held in a closed-cycle helium cryostat. The temperature was varied from 13 K to room temperature in intervals of ~ 10 K. At each temperature, the magnetic field was varied from 0.2 kG to 5 kG in steps of ~ 0.3 kG.

Constant temperature and magnetic field Hall measurements were performed at room temperature using a 1 kG magnetic field.

**4.2. Optical Microscopy**

In this study calibration layers of GaSb and GaInSb were grown with the aim of optimizing the growth parameters of the respective materials in terms of surface morphology. A Nomarski interference contrast microscope was used to study the surfaces of the calibration layers.
The thickness, and hence the growth rate, of the calibration layers was also determined using a Nomarski interference contrast microscope. The calibration layers grown on the GaAs substrates were cleaved and etched with Murakami etchant (10 g potassium ferricyanide, 10 g sodium hydroxide, and 100 ml de-ionized water). Murakami etchant preferentially etches the interface between the substrate and the layer because of the high density of misfit dislocations in this region. This leaves behind a fine line that is visible with the Nomarski microscope.

### 4.3. Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy was used to characterize GaInSb/GaSb QW structures that were grown by MOCVD. The PL system used in this study is depicted in Figure 4.1.

![Schematic of the PL system used in this work.](image)

Samples were loaded in a closed-cycle helium cryostat, and the spectra were recorded at a temperature of 11 K. The 514.5 nm line of an Ar\(^+\) laser was used as an excitation source. The laser beam was focused onto the sample using a horizontally adjustable
mirror. The PL emitted by the sample was focused onto the entrance slit of a spectrometer by a condenser lens, and a high-pass filter placed in front of the entrance slit to the spectrometer was used to remove the reflected laser beam. The PL signal was detected by a liquid nitrogen cooled Ge photodetector. The laser power used was 4 mW.

### 4.4. Transmission Electron Microscopy

A Philips CM20 transmission electron microscope (TEM) operating at 200 kV was used to study GaInSb/GaSb QW structures that were grown by MOCVD.

Cross-sectional TEM samples of selected QW structures were prepared for analysis as outlined in Figure 4.2. Two 2×3 mm rectangles are cut from the original sample using a diamond saw. These two rectangles are then glued together using Gatan glue, with their growth surfaces touching. A 2×3 mm GaAs rectangle is glued on either side of the two sample rectangles for support. All sample rectangles, including the GaAs supports, are ~0.5 mm thick – the standard thickness of commercially supplied semiconductor wafers. One surface of the resulting 3×2 mm sample is mechanically thinned using 1200 grid sanding paper and then polished using a 1 µm alumina polishing suspension. A 30 µm thick copper grid is glued onto the polished side. The non-gridded side is then thinned with sanding paper until the sample is ~30 µm thick, and is then polished using alumina suspension. A tiny hole (~200 µm in diameter) is milled across the interface where the two growth surfaces meet with the use of an argon ion mill. TEM is performed on the region of thin material surrounding the hole.

![Figure 4.2: The making of a cross-sectional TEM sample.](image-url)
TEM images were obtained under two-beam conditions with \( \mathbf{g} = [200] \). The \( \mathbf{g} \) vector was chosen so that the diffraction contrast between GaSb and GaInSb would be at a maximum. This was done by considering the structure factor of the zinc-blende structure (Table 4.1) since \( \text{Ga}_{1-x}\text{In}_x\text{Sb} \) crystallizes in this structure. The structure factor is the main factor determining the intensity of the diffracted beam, and from Table 4.1 it is seen that the (200) beam reflection will result in a structure factor of \( |F|^2 = 16 \left( f_{Ga} - f_{Sb} \right)^2 \) for GaSb and a structure factor of \( |F|^2 = 16 \left( (1-x)f_{Ga} + x f_{In} - f_{Sb} \right)^2 \) for \( \text{Ga}_{1-x}\text{In}_x\text{Sb} \). Since the group V contribution to the structure factor is a minimum at this reflection, a change in the group III contribution will have a more notable effect on the resulting structure factor than when the group V contribution is more dominant. Thus, the (200) beam reflection is expected to give maximum contrast between the two materials. Here, \( f \) denotes the atomic scattering factor, and is used to describe the efficiency of scattering of a specific atom in a given direction.

| \((h + k + l)\) | Example | \(|F|^2\) |
|-----------------|---------|------------|
| Odd             | 111     | \(|F|^2 = 16 \left( f_{III} + f_{V} \right)^2 \) |
| Odd multiples of 2 | 222, 200 | \(|F|^2 = 16 \left( f_{III} - f_{V} \right)^2 \) |
| Even multiples of 2 | 220, 400 | \(|F|^2 = 16 \left( f_{III} + f_{V} \right)^2 \) |

### 4.5. X-Ray Diffractometry

The composition of the \( \text{Ga}_{1-x}\text{In}_x\text{Sb} \) calibration layers grown on GaSb substrates was determined with the use of a Philips PW 1840 X-ray diffractometer and CuK\(_{a1} \) (\( \lambda = 1.5405 \) Å) radiation. The peak position \((2\theta)\) of the 400 Bragg reflection of a \( \text{Ga}_{1-x}\text{In}_x\text{Sb} \) layer is substituted into Bragg’s law to obtain the inter-planar spacing \((d)\) of the alloy. Bragg’s Law is given by the well known formula:
\[ 2d \sin \theta = \lambda \] 4.1

From this, the lattice parameter (a) of the alloy can be determined, since

\[ d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \] 4.2

where \((h k l) = (4 0 0)\).

The lattice parameter of the alloy can then be used to determine the composition of the alloy by using Vegard’s law:

\[ a = (1 - x)a_{GaSb} + xa_{InSb} \] 4.3

The lattice parameters of the constituent binaries are given in Appendix A. The diffractometer gave a resolution of 0.02 ° 2θ.
Chapter 5: Development of GaInSb Nano-Layers

As a first step towards developing InAs/GaInSb strained-layered superlattices, an attempt is made to achieve the nano-scale (~100 Å) growth of GaInSb. This task is approached by first optimizing the growth of relatively thick (~2 µm) epitaxial films, and then assuming similar growth parameters during nano-scale deposition. Due to the limitations of conventional TEM and XRD in relation to resolution and sensitivity, the structural characterization of a single nano-scale epitaxial layer in terms of deposition rate, growth mode, and indium incorporation, cannot be determined. For this reason, GaInSb layers were grown as part of a GaInSb/GaSb quantum well (QW) structure. By using this approach, the GaInSb QW’s (~100 Å) could be characterized with the use of photoluminescence spectroscopy, which, when used in conjunction with TEM and/or XRD, proves useful in the analysis of such small scale deposition.

This chapter consists of four main sections. The first section discusses strained-layer epitaxy and the structural limitations and considerations associated with quantum well design and deposition. Section two deals with the band alignment of GaInSb/GaSb quantum well structures and illustrates how, with the use of photoluminescence spectroscopy, TEM and/or XRD, GaInSb nano-layers are characterized in this study. The preliminary growth needed for quantum well deposition is laid out in section three, with the final results being summarized in the concluding section on quantum well design, deposition and characterization.

Unless otherwise stated, all symbols and material parameters used in this chapter are given in Appendix A.

5.1. Strained-Layer Epitaxy

Epitaxy is the phenomenon in which a single crystalline substrate imposes the same
orientation on a single crystal grown on the substrate by deposition. **Hetero-epitaxy** results when the substrate and epilayer constitute different materials and, as a result, have different lattice parameters. This lattice mismatch introduces misfit dislocations which degrade the quality of the epilayer material near the interface region. In **strained-layer epitaxy**, however, lattice misfit is accommodated by strain. This effect is illustrated in Figure 5.1.

![Figure 5.1: Illustration of strained-layer epitaxy](image)

If the epilayer is sufficiently thin, a strained system is lower in energy than a relaxed system and so pseudomorphic growth results. This physical deformation of the crystal leads to a distortion of the atomic locations, which in turn affects the band structure of the strained material. As a result, the band alignment of a strained-layer structure can be engineered to meet a given requirement. It is this phenomenon that is exploited in QW and SLS structures.

It follows that for pseudomorphic growth to result, layers have to be thinner than a certain critical thickness, above which misfit dislocations will be introduced. Additionally, to ensure spatial uniformity of band alignment, interface roughness should be reduced to a minimum. An elementary introduction to epitaxy is given by van der Merwe (van der Merwe, 2002).
5.1.1. Critical Thickness

Various attempts have been made at determining the critical thickness of a strained-layer. Work done by van der Merwe (van der Merwe, 1963), Matthews and Blakeslee (Matthews and Blakeslee, 1974), and People and Bean (People and Bean, 1985), is most commonly referenced on this matter.

Matthews and Blakeslee approached the problem from a mechanical equilibrium point of view, and postulated that, if the force exerted on an existing threading dislocation by misfit stress exceeds the tension in the dislocation line, then the dislocation can elongate in the plane of the interface, producing a misfit dislocation line. This effect is illustrated in Figure 5.2 for a single overlayer.

Figure 5.2: Elongation of an existing threading dislocation to form a length \( LL' \) of misfit dislocation line. When the strain force \( F_S \) exceeds the tension in the dislocation line \( F_D \) a misfit dislocation line is generated. The overlayer thickness \( h_a \) at which \( F_S = F_D \) is the critical thickness, above which misfit dislocations are introduced.

In the work done by van der Merwe and People and Bean, an energy approach was used. In both cases, the critical thickness was obtained by equating the strain energy density with a minimum energy density required for the generation of dislocations. This minimum energy was assumed by van der Merwe to be the interfacial energy between the
film and substrate, while People and Bean used the energy density associated with an isolated screw dislocation.

The critical thickness for a GaInSb/GaSb QW is plotted in Figure 5.4, as a function of composition. Here, the models of both Matthews and Blakeslee, and People and Bean are used. The associated expressions for critical layer thickness are given below for a single overlayer, where $a$ is the overlayer lattice parameter, $a_0$ is the substrate lattice parameter, $\alpha$ is the angle between the dislocation line and its Burgers vector, and $\lambda$ is the angle between the slip direction and the direction in the film plane perpendicular to the line of intersection of the slip plane and the interface. For a 60° dislocation, $\alpha = \lambda = 60^\circ$, while for a pure edge dislocation $\alpha = 90^\circ$ and $\lambda = 0^\circ$.

Matthews and Blakeslee:

$$ h_c = \left( \frac{b}{8\pi f} \right) \left[ \frac{1 - \nu \cos^2 \alpha}{(1 + \nu) \cos \lambda} \right] \left[ \ln \left( \frac{h_c}{b} \right) + 1 \right] $$

Figure 5.4: Critical layer thickness for a GaInSb/GaSb QW as a function of Indium content.
People and Bean: \[ h_c = \left( \frac{1 - \nu}{1 + \nu} \right) \left( \frac{1}{16\pi \sqrt{2}} \right) \left( \frac{b^2}{a} \right) \left( \frac{1}{f^2} \right) \ln \left( \frac{h_c}{b} \right) \]  

where

\[
\text{Poisson’s Ratio: } \nu = \frac{C_{12}}{C_{11} + C_{12}} \]

Misfit: \[ f = \frac{a - a_0}{a_0} \]

Burgers vector: \[ b = \frac{a}{\sqrt{2}} \]

Considering the model of Matthews and Blakeslee, for a QW with a thickness less than that of the barrier layers a critical thickness is reached when the strain force is twice the tension in the dislocation line, and thus the critical thickness of a QW is twice that of a single overlayer. This doubling of the critical layer thickness for QW’s is illustrated in Figure 5.3, and has been taken into account when generating both the Matthews and Blakeslee and the People and Bean curves in Figure 5.4.

From Figure 5.4 it is seen that the simulations obtained using the equation of Matthews and Blakeslee show critical layer thickness values that are, in general, significantly lower than those predicted by People and Bean. For (001) epitaxial zinc-blende systems it is generally observed that misfit strain is accommodated by the formation of 60° misfit dislocations when the misfit is low, while pure edge dislocations are more dominant in high misfit systems (Fitzgerald, 1993). Despite this knowledge, the critical layer thickness obtained from pure edge dislocation considerations is used in this work, with the aim of erring on the safe side.
5.1.2. Interface Roughness

Since the band alignment of a strained-layer system sensitively depends on layer thickness, a rough interface morphology will result in QW’s with a spatially varying band structure throughout the interface plane (Figure 5.5). This spatial non-uniformity in band structure, and hence material properties, is undesirable, and must be kept to a minimum. Two factors influencing interface quality is the growth mode of constituent layers, and the choice of substrate.

Growth Mode

Fundamentally, epitaxial growth is either two-dimensional – in which case layer-by-layer deposition results, three-dimensional – in which case island formation results, or a combination of the two – in which case deposition is initially two-dimensional and later converts to three dimensional growth (van der Merwe, 2002). These different growth modes, known respectively as Frank-van der Merwe, Volmer-Weber, and Stranski-Krastanov growth modes, are shown in Figure 5.6.

Apart from the degree of lattice mismatch, the type of growth mode depends strongly on
the growth conditions of a material. Growth parameters such as substrate temperature, V/III ratio, vapour phase composition of reagents, and growth rate, all contribute to the resulting growth mode.

The surface morphology of thick (~2 µm) epitaxial layers gives an indication of the growth mode associated with a given set of growth parameters in the absence of strain. Here, the surface morphologies of thick calibration layers are used to optimize the conditions of GaInSb and GaSb growth, with the awareness that these results may differ in the case of strained nano-layers.

**Substrate Choice**

Another factor that influences growth mode and material quality is the choice of substrate; firstly, with regard to the substrate material and, secondly, with regard to the orientation of the substrate. Due to the mismatch between the lattice constant of the substrate and the average lattice constant of a QW structure, there is a limit to the overall thickness of a QW structure after which misfit dislocations are introduced at the substrate/structure interface. For this reason, GaSb is the best choice of substrate for GaInSb/GaSb QW structures, as it introduces the lowest amount of lattice misfit. This is illustrated in Table 5.1, where the lattice misfit (equation 5.4) at the substrate/structure interface is shown for four common III/V semiconductor substrates. A Ga$_{0.8}$In$_{0.2}$Sb/GaSb QW structure, with a 1:1 thickness ratio, has been assumed in the calculations. The lattice constants of the substrates are given in Appendix A.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Misfit (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>8.5</td>
</tr>
<tr>
<td>InAs</td>
<td>1.3</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.6</td>
</tr>
<tr>
<td>InSb</td>
<td>5.3</td>
</tr>
</tbody>
</table>

The orientation of the substrate also influences the growth mode of deposition. In this work, QW structures are grown simultaneously on both (100) and 2°off (100) GaSb (Te) substrates to study the influence of substrate orientation on the interface quality of QW structures. Since rough interfaces will result in broad PL peaks, it follows that the full-width at half-maxima (FWHM) of PL peaks can be used as a measure of interface quality in QW structures.
5.2. GaInSb/GaSb Quantum Well Structures

In pseudomorphically grown heterostructures, lattice mismatch is accommodated by strain. This physical deformation of the crystal leads to a distortion of the atomic locations, which in turn affects the band structure of the strained material (Donati, Kaspi and Malloy, 2003). This effect is illustrated to scale in Figure 5.7 for a Ga$_{0.8}$In$_{0.2}$Sb/GaSb hetero-interface. Here, the energy bands have been drawn with respect to the InSb valence band.

For unstrained material, the difference in valence band and conduction band energies of GaSb with respect to GaInSb is simply given by:

$$\Delta E_{v0} = VBO_{GaSb} - VBO_{GaInSb}$$

5.6
\[ \Delta E_{e0} = E_{g,GaSb} - E_{g,GaInSb} + \Delta E_{v0} \]  

When GaInSb is *pseudomorphically* deposited on bulk GaSb, however, the relationships between band edges have to be adjusted to include the effects of strain and heavy hole-light hole (HH-LH) splitting.

The strain experienced by the GaInSb layer in the interfacial plane is assumed to be isotropic, and is given by

\[ \varepsilon_{xx} = \varepsilon_{yy} = \frac{a_{GaSb} - a_{GaInSb}}{a_{GaInSb}} \]

where \( x \) and \( y \) denote Cartesian coordinates in the interfacial plane. The strain along the growth direction is given by

\[ \varepsilon_{zz} = -2 \frac{C_{12}}{C_{11}} \varepsilon_{xx} \]

The band offsets including strain and HH-LH splitting are given below. All symbols are as defined in Appendix A.

\[ \Delta E_c = \Delta E_{e0} - a_c \left( \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \right) \]

\[ \Delta E_{v, hh} = \Delta E_{v0} - a_v \left( \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \right) - \frac{b}{2} \left( \varepsilon_{xx} + \varepsilon_{yy} - 2 \varepsilon_{zz} \right) \]

\[ \Delta E_{v, lh} = \Delta E_{v0} - a_v \left( \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \right) + \frac{b}{2} \left( \varepsilon_{xx} + \varepsilon_{yy} - 2 \varepsilon_{zz} \right) \]

From Figure 5.7 it can be seen that the GaInSb LH valence band falls below the GaSb valence band maximum in energy, while the HH valence band shifts up in energy with respect to the GaSb valence band maximum. It follows that the well depths in a GaInSb/GaSb QW structure are given by \( \Delta E_c \) and \( |\Delta E_{v, hh}| \).
As an example, the band alignment of a Ga$_{0.8}$In$_{0.2}$Sb/GaSb QW structure is shown in Figure 5.8. The GaInSb LH valence band is now below the GaSb valence band in energy and is no longer of interest.

The resulting strained GaInSb band gap is thus given by

\[ E_{\text{strained}} = E_{g, \text{GaSb}} - \Delta E_c + \Delta E_v \]  

5.13

5.2.1. Quantum Confinement

When a photon of energy \( E_{\text{photon}} \geq E_{g, \text{GaSb}} \) excites an electron in the GaSb barrier material, the generated electron-hole pair becomes trapped in the GaInSb QW (Figure 5.8). The electron becomes trapped in a potential well with barrier height \( V = \Delta E_c \) and width \( L_c \), while the hole becomes trapped in a potential well of height \( V = |\Delta E_{\text{v, hh}}| \) and width \( L_c \). From elementary quantum theory it is known that when a particle is trapped in a
potential well with a barrier height $V$, and with a well width $L_z$ being very small, then the energy $E$ of the particle is quantized. That is, the confinement of the particle leads to restrictions on its wave function that allow the particle to have certain specific energies and no others (Beiser, 2003).

The energies of such a confined particle can be obtained by solving Schrödinger’s steady-state equation for a finite potential well. The latter has two solutions, and these are given below:

**Symmetric:** $\tan \left( k_2 \frac{L_z}{2} \right) = \frac{k}{k_2}$ \hspace{1cm} (5.14)

**Anti-symmetric:** $\cot \left( k_2 \frac{L_z}{2} \right) = -\frac{k}{k_2}$ \hspace{1cm} (5.15)

where $k = \sqrt{\frac{2m(V - E)}{\hbar^2}}, \quad k_2 = \sqrt{\frac{2mE}{\hbar^2}},$ and $m$ is either the electron or hole effective mass depending on which is being considered (Zettili, 2004). These two solutions describe two different types of states. The first describes symmetric states, while the second describes antisymmetric states. Since excited electrons and holes relax to their lowest energy state before recombining, only the ground state energy is of interest, and is denoted as $E_e$ and $E_h$ for electrons and holes respectively. The ground state energy level is a symmetric state and thus only the first solution is of interest. It follows, that the energy released when the electron-hole pair recombines is given by

$$E_{\text{recom}} = E_{\text{strained}} + E_e + E_h$$ \hspace{1cm} (5.16)

### 5.2.1. Photoluminescence Spectroscopy

From preceding sections, it is seen that the bandgap, $E_{\text{strained}}$, of a $\text{Ga}_{1-x}\text{In}_x\text{Sb}$ QW layer depends on $x$, while the recombination energy, $E_{\text{recom}}$, of an electron-hole pair in a QW
depends on both \( x \) and the well width \( L_z \). In the PL analysis of GaInSb/GaSb QW structures the 514.5nm Ar\(^+\) laser line is used to excite electrons in the GaSb valence band to above the conduction band. When these electron-hole pairs recombine in the GaInSb QW, the energy of emitted photons, excluding the exciton binding energy, is given simply by

\[
E_{PL} = E_{recom}
\]

Using the theory laid out in the preceding sections, the PL energy as a function of well width was simulated and is plotted in Figure 5.9 for GaInSb/GaSb QW’s of different compositions. If the In content of a grown QW is known from XRD analysis of a GaInSb calibration layer, then a simulation of PL energy as a function of well width for this composition can be used to determine the well width of the QW. This is achieved by placing the measured PL energy of the QW on the curve and reading off the well thickness that corresponds to that point on the curve. Conversely, if the well width of the

Figure 5.9: PL energy of a GaInSb/GaSb QW as a function of well thickness. The relationship is plotted for various In quantities. A temperature of 10 K is assumed.
structure is known from TEM analysis, then such a curve can be used to determine the In content of a grown QW.

Thus, coupled with TEM and/or XRD, photoluminescence spectroscopy becomes a simple, non-destructive means of determining composition and thickness parameters in a quantum well system, and hence a convenient means of characterizing the nano-scale deposition of GaInSb. In addition, as previously discussed, the FWHM of PL peaks give an indication of interface roughness, and hence can be used to obtain qualitative information on the growth mode of GaInSb layers on the nano-scale.

5.3. Preliminary Growth

In preparation for the deposition of GaInSb/GaSb QW’s, calibration layers (~2 µm) of GaSb and GaInSb were grown. The growth temperature throughout this work was kept at 550 °C. The choice of growth temperature was based on previous studies on the optimization of growth parameters for GaSb and GaInSb by Irving Brown (Irving Brown, 2000) and Vankova (Vankova, 2002), respectively. These studies were carried out on the growth system used in this work. Since the time delay between the deposition of successive layers in a QW structure is of the order of a few seconds, the choice of growth temperature for GaSb and GaInSb needs to be the same. Literature predicts that at 550 °C TMGa and TMSb are only partially dissociated, and that the incorporation of indium in the deposition of GaInSb is more efficient (3.1.4). Furthermore, the lower availability of Ga and Sb in the vapour phase lowers the overall growth rate of GaInSb and GaSb (3.1.4). These predictions were observed by Vankova and Irving Brown. In addition, the work done by Vankova and Irving Brown showed that layers of reasonable surface quality can be grown at 550 °C. For this reason the growth temperature of 550 °C was chosen, since it allows for more freedom in terms of In incorporation, while lowering the growth rate of the material. The surface morphology of epilayers is expected to improve with a decrease in growth rate. This was shown by Irving Brown for the growth of GaSb epilayers.
The purpose of these calibration layers was twofold. Firstly the V/III ratio of GaSb and GaInSb was optimized in terms of surface morphology in order to determine the growth parameters most likely to produce QW’s with good interface quality. Secondly, the resulting growth rate and In incorporation at the optimum V/III ratio was determined and used as a guide in QW design.

The latter was carried out for two different In vapour phase compositions at two different growth rates.

### 5.3.1. Growth Procedure

In this work, samples were grown by Metal Organic Chemical Vapour Deposition. This technique has been discussed in Chapter 3. Outlined below, is the growth procedure followed for the deposition of calibration layers. The growth of all calibration layers was carried out simultaneously on both GaSb(Te) and GaAs substrates orientated at 2° off the (100) towards (111)B.

- Before being loaded into the reactor, the GaAs substrate was blown clean with nitrogen. The GaSb substrate, however, was first degreased by consecutive submersion in heated trichloroethylene, acetone and methanol, and then etched to remove native oxides. It was then blown dry with nitrogen and loaded into the reactor. The removal of GaSb oxide layers has been considered by many authors (Vineis, Wang and Jensen, 2001; Papis-Polakowska, 2006; Tessler et. al., 2006; Weiss et. al., 2007). Here, the GaSb substrates were etched in hydrochloric acid (37 %) for 5 minutes, and then rinsed in methanol. Throughout the substrate preparation process the exposure of the GaSb substrate to air was limited to prevent the reintroduction of surface impurities and oxides.
- Before growth, any residual oxide still present on the GaSb substrate was thermally removed by annealing the substrates at 650 °C for 15 minutes while allowing hydrogen to flow through the reactor.
- During the substrate annealing step, hydrogen was directed through the precursor bubblers out to vent, in order to stabilize the precursor flow rates.
- After the annealing step, the temperature was lowered to 550 °C and growth was commenced by simultaneously introducing all the precursors into the reactor.
- After deposition the precursors were simultaneously removed from the reactor, and the heater was turned off.
- Hydrogen was sent through the reactor while the samples cooled.

### 5.3.2. Summary of Calibration Layers

The growth parameters of the GaSb and GaInSb calibration layers are summarized in Table 5.2 and Table 5.3, respectively. The growth rate of the calibration layers was controlled by varying the TMGa MF. The V/III ratio of the respective series was varied by keeping the group III MF’s constant and varying the TMSb MF.

<table>
<thead>
<tr>
<th>TMGa MF</th>
<th>V/III</th>
<th>Average Growth Rate (Å/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7×10^{-4}</td>
<td>0.60, 0.71, 0.80, 0.99</td>
<td>16</td>
</tr>
<tr>
<td>9.3×10^{-5}</td>
<td>0.60, 0.70, 0.80</td>
<td>8</td>
</tr>
</tbody>
</table>

It was found that the surface morphology of all calibration series, regardless of growth rate and In content, follows the same trend as the V/III ratio is varied. This change in surface morphology with V/III ratio is shown in Figure 5.10, using GaSb as an example. No representative for a V/III of 0.5 is shown as no two surface morphologies at this V/III ratio were the same, with two of them appearing non-stoichiometric. The origin of this unpredictability is unknown.

In zinc-blende materials, growth on misoriented {100} surfaces shows anisotropic growth rates along the two primary <110> directions (Asai, 1987; Fukui and Saito, 1988; Fukui et. al., 1992; Kasu and Kobayashi, 1993). Asai showed that for GaAs, the growth rate
along the \(<110>\) direction is higher than along the \(<\bar{1}10>\) direction under As-rich conditions at typical growth temperatures \((550 \, ^\circ\text{C} < T < 750 \, ^\circ\text{C})\). This phenomenon is observed here for GaSb and GaInSb in the V/III dependence of surface morphology shown in Figure 5.10, where the shape of surface features change from circular to an elongated form as the V/III ratio is increased. Here, a V/III ratio in the range 0.6 - 0.7 is considered for QW deposition. This small optimum V/III range is due to the low vapour pressure of antimony (section 3.1.2).

From Table 5.3 it is seen that the content of indium in the solid increases slightly with increasing V/III ratio. There also appears to be an increase in the incorporation of In with a decrease in growth rate. The increase in the incorporation efficiency of In with a decrease in the TMGa MF is a result of the associated decrease in growth rate of the binary component GaSb (section 3.1.4). An increase in the incorporation of In with an
increase in V/III ratio implies that the atomic V/III at the growth interface is in fact below unity (section 3.1.4), since there appears to be competition between the Ga and In atoms for placement on the group III sublattice.

Table 5.3: Summary of GaInSb calibration layers.

<table>
<thead>
<tr>
<th>TMGa MF</th>
<th>V/III</th>
<th>x (%)</th>
<th>(x_r) (%)</th>
<th>Growth Rate (Å/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8×10^-4</td>
<td>V/III 0.50</td>
<td>14</td>
<td>7.5</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.91</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.99</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.7×10^-4</td>
<td>V/III 0.50</td>
<td>?</td>
<td>12.5</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.01</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.6×10^-5</td>
<td>V/III 0.51</td>
<td>14</td>
<td>7.5</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>0.61</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>16</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.82</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.91</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.01</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.1×10^-5</td>
<td>V/III 0.50</td>
<td>23</td>
<td>12.5</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The resulting growth rates of the TMGa MFs studied are ~ 17 Å/s and ~ 9 Å/s, and the resulting indium content in the solid for the vapour phase compositions studied are ~ 15 % and ~ 23 %. From Figure 5.4 it is seen that for an In content in this range, the critical thickness of GaInSb QW’s is in the region of 100 Å (assuming pure edge misfit dislocations – section 5.1.1). Thus, for the 17 Å/s and 9 Å/s growth rates, the maximum allowed deposition time in order to avoid the introduction of misfit dislocations is only 6 and 11 seconds, respectively. Therefore, to maximize the deposition time of subsequent QW’s, only the lower growth rate was considered in this study.

In order to allow the deposition of QW structures to proceed smoothly, the need to adjust precursor flow rates between the deposition of successive GaSb and GaInSb layers was eliminated by keeping the TMGa and TMSb MFs the same for the deposition of both GaSb and GaInSb. Additional calibration layers were thus grown. Based on the initial set of calibration layers, the V/III of the new layers was limited to the range 0.6 – 0.7. Two GaInSb layers of different compositions were grown. For each GaInSb layer a GaSb layer was grown with the same TMGa and TMSb MF’s used in the deposition of the GaInSb
layer. The growth parameters and resulting In content and growth rate of these layers are summarized in Table 5.4. These results were used in the design and analysis of QW structures.

### Table 5.4: Growth parameters for QW deposition.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Ga MF</th>
<th>$x_v$ (%)</th>
<th>V/III</th>
<th>$x$ (%)</th>
<th>Growth Rate (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>9.3x10^-5</td>
<td>-</td>
<td>0.66</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>S2</td>
<td>9.2x10^-5</td>
<td>-</td>
<td>0.69</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>GaInSb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>9.2x10^-5</td>
<td>7.5</td>
<td>0.61</td>
<td>12.7</td>
<td>9</td>
</tr>
<tr>
<td>S2</td>
<td>9.2x10^-5</td>
<td>12.5</td>
<td>0.60</td>
<td>20.4</td>
<td>10</td>
</tr>
</tbody>
</table>

### 5.4. Quantum Well Design, Deposition and Characterization

#### 5.4.1. Quantum Well Design

Two QW structures were grown, one based on an $x_v$ of 7.5 % (S1) and the other on an $x_v$ of 12.5 % (S2). The growth parameters used in the deposition of structures S1 and S2 are summarized in Table 5.4. Using the method laid out in section 5.2.1, the PL energy as a function of well thickness for both well compositions was simulated (Figure 5.11), and used as an aid in designing the QW structures. The design of these structures, in terms of quantum well thickness, was limited by three main factors viz. critical thickness, PL detection limitations, and growth rate limitations (Figure 5.11). Critical thickness has been discussed in section 5.1.1, and Figure 5.4 shows that the critical thickness for both compositions lies in the region of 100 Å (assuming pure edge misfit dislocations – section 5.1.1). Thus, 100 Å was considered an upper limit for well thickness. As mentioned in section 4.3, a germanium detector was used to detect photoluminescence.
from the sample. This detector has a lower limit of detection at about 0.72 eV, which further limited the choice in well thickness for the structure with an In content of 20.4% to below 75 Å. Finally, Table 5.4 shows that the growth rate of the constituent materials is \(~9\) Å/s.

Figure 5.11: Design limitations of QW structures.

Figure 5.12: Generic design of QW structures. Thicknesses A > B > C > D in thickness.
It was not considered practical to grow for less than 3 seconds, and thus from a growth rate point of view, a lower limit of ~ 30 Å was placed on well thickness.

The generic design of these structures is shown in Figure 5.12. The structures were designed to consist of a 3000 Å buffer layer followed by four QW’s (A > B > C > D in thickness) separated by 1000 Å barrier layers, and capped with a 1000 Å capping layer. The well thicknesses and associated PL energies that were aimed for in the design of these structures are given in Table 5.5 and Table 5.6 for structures S1 and S2, respectively.

5.4.2. Growth Procedure

The growth procedure followed for the deposition of QW structures differs from that followed for the growth of calibration layers only in the substrates used and in the incorporation of growth interruption steps between the constituent layers of QW structures. The growth interruption procedure was such that after the deposition of one of the constituent layers, all the precursors were simultaneously removed from the reactor. This was followed by a three second delay during which only hydrogen was sent through the reactor, after which the precursors required for the deposition of the subsequent layer were simultaneously introduced into the reactor. This was done in order to flush the reactor of reagents between growth steps and, in so doing, minimize compositional grading at the interfaces. Here, each structure was grown simultaneously on a (100) and a 2° off (100) GaSb(Te) substrate.

As previously mentioned, in order to allow the deposition of QW structures to proceed smoothly, the TMGa and TMSb MFs were kept the same for the deposition of both GaSb and GaInSb. Thus, throughout the deposition of QW structures the precursor flow rates were kept constant, and precursors could simply be switched in and out of the reactor as needed.
5.4.3. Results and Analysis

The PL spectra of structures S1 and S2 are given in Figure 5.14 and Figure 5.15, respectively. The structures were grown on both (100) and 2° off (100) GaSb(Te) substrates. This was done in order to study the influence of substrate orientation on the interface quality of QW structures (section 5.1.2). In each figure, the PL spectrum of a GaSb calibration layer is given together with spectra from both (100) and 2° off (100) GaSb(Te) substrate material. The spectra were deconvoluted with the use of spectral analysis software (PeakFit v4.04), and the Gaussians that best fit the spectra are indicated by dashed lines. The measured PL peak energies together with their FWHM for structures S1 and S2 are given in Table 5.5 and Table 5.6, respectively.

In order to determine the possible contribution of PL from the GaSb barrier layers to the PL spectra of the QW structures, the PL from the GaSb calibration layers is first considered. The PL spectrum of a GaSb calibration layer is shown in Figure 5.13. The line appearing at 800 meV is generally ascribed to bound exciton recombination (Woelk and Benz, 1974; Rühle et al., 1976; Chen and Su, 1989; Su and Chen, 1993; Iyer et. al., 1994; Gladkov et. al., 1995; Salesse et. al., 1997). However, this line has also been
Figure 5.14: Photoluminescence of QW structure S1. The spectra were deconvoluted with the use of spectral analysis software (PeakFit v4.04), and the Gaussians that best fit the spectra are indicated by dashed lines. The solid lines represent the measured spectra. The spectra have been normalised.

Table 5.5: Results summary for QW structure S1.

<table>
<thead>
<tr>
<th></th>
<th>Aimed for:</th>
<th>Measured:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (Å)</td>
<td>PL Energy (eV)</td>
<td>PL Energy (eV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>A</td>
<td>99</td>
<td>0.749</td>
</tr>
<tr>
<td>B</td>
<td>72</td>
<td>0.761</td>
</tr>
<tr>
<td>C</td>
<td>54</td>
<td>0.772</td>
</tr>
<tr>
<td>D</td>
<td>36</td>
<td>0.786</td>
</tr>
<tr>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 5.15: Photoluminescence of QW structure S2. The spectra were deconvoluted with the use of spectral analysis software (PeakFit v4.04), and the Gaussians that best fit the spectra are indicated by dashed lines. The solid lines represent the measured spectra. The spectra have been normalised.

Table 5.6: Results summary for QW structure S2.

<table>
<thead>
<tr>
<th></th>
<th>Aimed for:</th>
<th>Measured:</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness (Å)</td>
<td>PL Energy (eV)</td>
<td>Thickness* (Å)</td>
<td>PL Energy (eV)</td>
<td>FWHM (meV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>100</td>
<td>2° off</td>
<td>100</td>
<td>2° off</td>
</tr>
<tr>
<td>A</td>
<td>60</td>
<td>0.732</td>
<td>65 ± 10</td>
<td>0.760</td>
<td>0.759</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td>50</td>
<td>0.743</td>
<td>42 ± 10</td>
<td>0.769</td>
<td>0.768</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>C</td>
<td>40</td>
<td>0.756</td>
<td>39 ± 10</td>
<td>0.779</td>
<td>0.777</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>D</td>
<td>30</td>
<td>0.771</td>
<td>-</td>
<td>0.785</td>
<td>0.786</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.745</td>
<td>-</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

* Thickness obtained from TEM micrograph (Figure 5.17).
ascribed to the recombination of a free electron with an unspecified neutral acceptor (Chidley et al., 1991), and to the recombination of a free electron with a hole bound to a neutral Si acceptor (Agert et al., 2002). The line appearing at 796 meV has been assigned to bound exciton recombination, and the line appearing at 778 meV is known as the “A-line”, and results from a free electron-to-native acceptor transition (Woelk and Benz, 1974; Rühle et al., 1976; Chen and Su, 1989; Su and Chen, 1993; Iyer et al., 1994; Gladkov et al., 1995; Salesse et al., 1997). The intensity of the A-line depends on the acceptor density and the crystal quality (Chen and Su, 1989). The native acceptor is the result of Ga vacancies and Ga antisites which form under Sb poor conditions (Jiang et al., 1995), and thus the intensity of this line gives a qualitative indication of the stoichiometry of a GaSb layer. From the relatively low intensity of this line in Figure 5.13, it is assumed that the layers grown in this study are of reasonably good stoichiometry.

From studying the PL spectra of both structures S1 and S2, there are no peaks that correspond to those observed for the GaSb calibration layer in position and width. It is thus concluded that the GaSb barrier material does not contribute to the observed luminescence. There does, however, appear to be a weak, but rather broad, contribution to the PL of these structures in the region of 800 meV. This contribution is more dominant for structures grown on 2°off (100) substrates, and has been labeled ‘S’ in the figures. From studying the PL spectra of the substrate material, it appears that these peaks may be the result of substrate contributions. This is especially clear for structure S2 grown on 2°off (100) substrate (Figure 5.15). Thus, it is concluded that the PL from structures S1 and S2 is largely due to QW luminescence.

For both structures S1 and S2, structures grown on the (100) substrate show the presence of four QW’s, labeled A, B, C, and D according to Figure 5.12. The structures grown on the 2°off (100) substrates, however, show the presence of “extra” peaks, labeled “X” and “Y” in the figures. The peak energies and FWHM of these peaks, together with the peak energies and FWHM of the QW peaks are given in Table 5.5 and Table 5.6. To determine the origin of these unexpected peaks, PL spectra were obtained from three
different positions, along the precursor flow direction, on the sample of structure S2 grown on the 2°off (100) substrate. These results are shown in Figure 5.16, and the three measuring positions are labeled “upstream” (i.e. closest to the reactor inlet), “middle”, and “downstream”. From many collective years of working on the growth system used in this study, it is known that layer thickness decreases along the precursor flow direction, with the thickest material being obtained closest to the reactor inlet. Thus, as the measuring position is moved further “downstream”, the QW’s are expected to decrease in thickness, and, according to Figure 5.9, a blue shift in the PL peak position of a given QW is expected. This effect is observed for all five peaks in Figure 5.16, and it is assumed that quantum size effects do play a role in the recombination giving rise to the “extra” peaks.

![Figure 5.16: Photoluminescence of the S2 QW structure grown on the 2°off substrate. The spectra have been normalised.](image)

As for the origin of these “extra” peaks, three possible explanations are strain induced spinodal decomposition (de Carvalho et. al., 1999), step bunching as a result of the mis-
orientation of the substrate (Botha and Leitch, 1996), and enhanced impurity incorporation due to the mis-orientation of the substrate. It is possible that these “extra”

Figure 5.17: Cross-sectional dark field TEM image of the S2 QW structure grown on the (100) GaSb(Te) substrate. Arrows point to the QW’s observed in this micrograph. The image was obtained under two-beam conditions with $g = 200$. Also shown, is the normalised PL spectrum of the S2 QW structure grown on the (100) GaSb(Te) substrate.
peaks may be paired with QW peaks, and that those associated with thinner QW’s may be hidden by the more intense PL coming from thicker QW’s. In either case, it appears that growth on non-vicinal substrates is more conducive to the deposition of high quality QW structures.

A typical TEM micrograph of the QW’s grown in this study is shown in Figure 5.17, using the S2 QW structure grown on the (100) substrate as an example. The PL spectrum of this structure is also included. The contrast between the QW and barrier material appears to be weak. Although the PL spectrum confirms the deposition of all four QW’s, only three of these QW’s are observed by TEM analysis. The average thicknesses of the QW’s were measured from the micrograph. A comparison of the nominal thicknesses and the measured thicknesses of these QW’s can be seen in Table 5.6. It is assumed that the observed QW’s correspond to the three thickest layers, and the measured thicknesses correspond well with the nominal thicknesses for these layers. The error in the measured thickness values is estimated to be ± 10 Å, taking into account the non-uniformity of QW interfaces as well as the dependence of the apparent QW thickness on the tilt angle of the sample in the microscope. From geometrical considerations, it follows that if a QW is not viewed exactly edge-on then it will appear to be thicker than what it really is. It thus follows that the structural analysis of thin (< 50 Å) QW’s, at least for the In content studied in this work, may not be readily obtainable using conventional TEM analysis. What has been shown, however, is that the measured QW thicknesses obtained from TEM analysis correspond well with the nominal thicknesses of these QW’s (Table 5.6), and, in the analysis that follows, the nominal QW thicknesses have been assumed to be a reasonably good approximation of the true QW thicknesses.

The PL energy as a function of well thickness was simulated and plotted in Figure 5.18 for various well compositions. Also plotted are the measured PL peak energies of the grown QW’s against their nominal thicknesses. Furthermore, for the S2 QW structure grown on the (100) orientated substrate, the measured PL peak energies of the QW’s against the measured thicknesses obtained from a TEM micrograph of the structure are
plotted. There appears to be a marked decrease in the expected incorporation efficiency of In. The predicted In content of structures S1 and S2 is 12.7 % and 20.4 %, respectively. What is observed however, is an In content of ~ 10.5 % and 14.5 %, respectively. This decrease in the expected incorporation of In is by far greater for the S2 QW structure, which had the higher nominal In content. A possible explanation for this observed incongruency in indium incorporation can be given by considering the effects of strain. Perhaps indium incorporates less efficiently in strained layers. This would explain the larger discrepancy in indium incorporation for the higher In content S2 structure.

Figure 5.18: Comparison of measured PL peak energies with simulated peak energies. The solid symbols represent data of the S1 QW structure, while the open symbols represent data of the S2 QW structure. Square symbols represent measurements taken from 100 substrates, while circles represent 2° off substrates. The PL peak energies are plotted against the predicted thickness in each case, except in the case of the open triangles. In this case, the PL peak energies of the 100 S2 structure is plotted against the measured thicknesses obtained from the TEM micrograph of the structure.
5.4.4. Concluding Remarks

Based on GaSb and GaInSb calibration layers, two QW structures, S1 and S2, were grown with a nominal In content of 12.7 % and 20.4 %, respectively. Each structure consisted of four QW’s of different thicknesses, and was simultaneously grown on both (100) and 2°off (100) GaSb(Te) substrates. The aim of this study was to firstly observe the nano-scale growth of GaInSb in terms of growth rate and In incorporation. Secondly, a comparison of substrate orientation was made, with the aim of determining the preferred substrate orientation for QW deposition. The results show that the nano-scale deposition of GaInSb was indeed achieved, and that the resulting growth rates of these layers approaches the nominal growth rates determined from GaInSb calibration layers. The In incorporation efficiency in nano-layers, however, was markedly lower than what was predicted by the GaInSb calibration layers. Regarding the choice of substrate orientation for QW deposition, the PL spectra of structures S1 and S2 show no significant difference in FWHM when comparing QW’s grown on the two types of substrates. The PL spectra of structures grown on the 2°off (100) substrate, however, show the presence of “extra” peaks which appear to be QW related, and could be the result of spinodal decomposition, step bunching, or enhanced impurity incorporation. Thus, it appears that growth on non-vicinal substrates is more conducive to the deposition of high quality QW structures.
Chapter 6: Electrical Characterization of Bulk InAs

In Chapter 5, the study of the MOCVD growth of GaInSb nano-layers as a first step towards the development of InAs/GaInSb strained-layered superlattices has been discussed. In the present chapter, the focus is shifted to the InAs component of the superlattice structure. The MOCVD growth of InAs is simplified by the binary nature of the compound and the high vapour pressure of arsine at typical growth temperatures. The former eliminates the need for alloy composition studies, while the latter significantly increases the range of V/III ratios that result in good solid stoichiometry (section 3.1.2). A previous study of the growth parameters of InAs has been carried out on the growth system used in this work (Vankova, 2005), and confirms the wide range of favorable InAs growth parameters. For this reason, the deposition of InAs is of only secondary concern in this chapter. What is of interest is the electrical characterization of InAs thin films.

Hall measurements is the standard technique used to electrically characterize semiconductor thin films. It is long known, however, that conventional Hall measurements cannot be used to accurately characterize InAs. This follows from the thickness (Wang et. al., 1992; Watkins et. al., 1995; Yamaguchi et. al., 1998; Wolkenberg et. al., 2000; Cai et. al., 2004) and magnetic field (Wieder, 1974; Wang et. al., 1992) dependence of Hall measurements carried out on InAs thin films, and the absence of carrier freezeout in temperature dependent Hall measurements (Meggitt et. al., 1980). These results are generally attributed to parallel conduction resulting from surface (Wieder, 1974; Noguchi et. al., 1991; Wang et. al., 1992; Olsson et. al., 1996; Piper et. al., 2006) and/or interface effects (Yamaguchi et. al., 1998; Wolkenberg et. al., 2000; Cai et. al., 2004; Okamoto et. al., 2005).

This chapter looks at extracting the surface and bulk electrical properties of n-type InAs thin films directly from variable magnetic field Hall measurements (Botha et. al., 2005; Krug et. al., 2007). This is achieved by employing the two-layer model of Nedoluha and
Koch (Nedoluha and Koch, 1952), and treating an InAs epilayer as consisting of two conductors connected in parallel viz. a surface and a bulk layer. For p-type InAs, the situation is complicated by the relatively large electron to hole mobility ratio of InAs which tends to conceal the p-type nature of InAs thin films from Hall measurements. Here, this effect is illustrated by way of theoretical simulation of Hall data (Botha, Shamba and Botha, 2008).

6.1. Charge Accumulation

Parallel conduction in InAs is generally attributed to the presence of surface (Wieder, 1974; Noguchi et. al., 1991; Wang et. al., 1992; Olsson et. al., 1996; Piper et. al., 2006) and/or interface (Yamaguchi et. al., 1998; Wolkenberg et. al., 2000; Cai et. al., 2004; Okamoto et. al., 2005) electron accumulation layers. The observation of electron accumulation at clean InAs free surfaces is well documented, and various techniques have been used to study this phenomenon (Wieder, 1974; Noguchi et. al., 1991; Wang et. al., 1992; Olsson et. al., 1996; Piper et. al., 2006). Findings show that a quantized (Noguchi et. al., 1991) electron accumulation layer (i.e. a two-dimensional electron gas) is present on all InAs surfaces, except for degenerately doped InAs, in which case, carrier depletion results at the surface (Piper et. al., 2006). The electron density resulting from such a surface accumulation depends reversibly on surface reconstruction (∼1×10^{12} \text{cm}^{-2} for As-stabilized surfaces, and <5×10^{11} \text{cm}^{-2} for In-stabilized surfaces) (Noguchi et. al., 1991), suggesting that surface accumulation is induced by donor-like intrinsic surface states, the density of which depends on the surface reconstruction. The density of surface states does not, however, depend on the p- or n-type nature of the underlying bulk material (Olsson et. al., 1996).

Interface charge accumulation, on the other hand, results from the formation of charge accumulating misfit dislocations, which accommodate the large lattice mismatch between InAs epilayers and GaAs substrates (Wolkenberg et. al., 2000). GaAs substrates are typically used for the measurements of the electrical properties of InAs epilayers, since
no semi-insulating (SI) InAs or GaSb substrates are available. Thus, the large lattice-mismatch between epilayer and substrate cannot be avoided.

For the purpose of this study, only surface charge accumulation is considered as a source of parallel conduction in InAs thin films.

### 6.2. Conventional Hall Measurements

As already mentioned, Hall measurements is the standard technique used to electrically characterize semiconductor thin films. By measuring the Hall voltage ($V_H$), the Hall coefficient ($R_H$) is obtained:

$$R_H = \frac{V_H d}{IB} \quad 6.1$$

where $d$ is the sample thickness, $I$ the current, and $B$ the magnetic field strength. Conventionally, the majority carrier concentration ($n$-electrons, $p$-holes) and mobility ($\mu$) of a thin film is determined from Hall coefficient and conductivity ($\sigma$) measurements, according to equations 6.2 and 6.3, respectively; where $q$ is the elementary charge.

$$n = \frac{r_H}{R_H q} \quad 6.2$$

$$\mu \approx \mu_H = |R_H| \sigma \quad 6.3$$

Here, $r_H$ is the Hall scattering coefficient and $\mu_H$ is the Hall mobility. The Hall scattering coefficient $r_H \approx 1$ for temperatures below 300 K (Schroder, 1998).
6.3. Shortfalls of Conventional Hall Measurements

6.3.1. Assumption 1 (parallel conduction):

Equations 6.2 and 6.3 assume uniform conduction and thus fall short in the analysis of InAs Hall data, since parallel conduction is not taken into account. The mobility of the underlying InAs layer (referred to here as the bulk layer) is significantly greater than that of the surface electron accumulation layer, and the carrier concentration of the surface layer is significantly higher than that of the bulk material (Wang et. al., 1992). It follows that surface properties shield the bulk properties in the conventional analysis of InAs Hall data by lowering the perceived mobility of a thin film, while increasing the perceived carrier concentration of the film.

6.3.2. Assumption 2 (mobility ratio):

For p-type InAs, conduction band contributions are not considered. Equation 6.2 is an approximation of the well known expression (Schroder, 1998),

\[
R_H = \frac{(p-b^2n)+(\mu_n B)^2(p-n)}{q\left((p+bn)^2 + (\mu_n B)^2(p-n)^2\right)}
\]

which shows that the Hall coefficient is in fact magnetic field dependent, and influenced by both hole and electron densities. Here, \(\mu_n\) is the electron mobility, and \(b = \mu_n / \mu_p\) is the electron to hole mobility ratio.

In InAs, \(b \approx 71.7\) (Meggitt et. al., 1980; Sze, 1981; Schroder, 1998) is large, and for n-type material, equation 6.2 is a good approximation. For p-type material, however,
equation 6.2 is no longer valid.

In summary, equations 6.2 and 6.3 assume uniform conduction from a single band, and thus fall short in the analysis of InAs Hall data, since parallel conduction is not taken into account and, for p-type InAs, conduction band contributions are not considered.

### 6.4. The Two-Layer Model

It is widely reported (Hongwei et. al., 1998; Kalem, 1990; Przeslawski et. al., 2000; Okamoto et. al., 2005; Gladkov et. al., 2006) that unintentionally doped InAs is n-type in nature. To extract meaningful information from conventional Hall data, unintentionally doped n-type InAs is treated as a two-layer system consisting of a bulk and a surface layer. This is done by employing the two-layer model of Nedoluha and Koch (Nedoluha and Koch, 1952), which approximates a two-layer system by two conductors connected in parallel. This two-layer system is illustrated in Figure 6.1. In the illustration, the applied electric field is in the negative x direction, while the applied magnetic field is in the positive z direction. The conductors with thicknesses \( d_b \) and \( d_s \) represent the bulk and surface layers, respectively, of an InAs epilayer. For the purpose of illustration, n-type InAs is considered, with \( n_b \ll n_e \). Since the conductors are connected in parallel, the Hall voltage induced across both conductors is the same. For both conductors, the Hall effect will cause electrons to move...
in the positive y direction and collect at the top of each conductor. Since the conductors are connected in parallel, and \(n_b \ll n_s\), the difference in charge accumulation at the top of each conductor will result in the clockwise flow of a compensation current \(i\).

The resulting Hall coefficient and magnetoresistivity as a function of magnetic field strength of such a two-layer system is given in equations 6.5 and 6.6, respectively; and an expression for the zero B-field conductivity is given in equation 6.7. The assignment of symbols is such that the subscript ‘s’ pertains to surface parameters, the subscript ‘b’ denotes bulk parameters, and the subscript ‘0’ indicates zero B-field parameters. Here, \(\rho\) denotes resistivity.

\[
R_H = \frac{(d_s + d_b)[(R_s \sigma_s^2 d_s + R_b \sigma_b^2 d_b) + R_s R_b \sigma_s \sigma_b^2 (R_b d_s + R_s d_b)B^2]}{(\sigma_s d_s + \sigma_b d_b)^2 + \sigma_b^2 (R_b d_s + R_s d_b)B^2} \tag{6.5}
\]

\[
\frac{\sigma_0 - \sigma}{\rho} = \frac{\rho - \rho_0}{\rho_0} = \frac{(R_s \sigma_s - R_b \sigma_b) \sigma_s \sigma_b d_s d_b B^2}{(\sigma_s d_s + \sigma_b d_b)^2 + \sigma_b^2 (R_b d_s + R_s d_b)B^2} \tag{6.6}
\]

\[
\sigma_0 = \frac{(\sigma_s d_s + \sigma_b d_b)}{d_s + d_b} \tag{6.7}
\]

It is assumed that the surface accumulation layer is always strongly n-type and thus, from equation 6.4, the surface layer Hall coefficient can be approximated by

\[
R_s = \frac{1}{qn_s} \tag{6.8}
\]

and the conductivity of the surface layer is given by

\[
\sigma_s = \mu_s n_s q \tag{6.9}
\]
Similarly, for n-type InAs the Hall coefficient and conductivity of the bulk layer can be expressed as

\[ R_b = \frac{1}{qn_b} \]  \hspace{1cm} 6.10

\[ \sigma_b = \mu_b n_b q \]  \hspace{1cm} 6.11

For p-type InAs, however, the large mobility ratio of InAs has to be taken into account, and the Hall coefficient and conductivity of a p-type bulk layer is expressed more generally as

\[ R_b = \frac{\left(p - b^2 n\right) + \left(\mu_n B\right)^2 (p - n)}{q\left[(p + bn)^2 + \left(\mu_n B\right)^2 (p - n)^2\right]} \]  \hspace{1cm} 6.12

\[ \sigma_b = \mu_n nq + \mu_p pq = \mu_n nq + (\mu_n / b) pq \]  \hspace{1cm} 6.13

The effective thickness of the accumulation layer is given by the screening length of the surface charge and is estimated by the Debye length \((L_D)\) (Wieder, 1974),

\[ d_s = L_D = \left(\frac{k_n \kappa \varepsilon_0 T}{q^2 (p + n)}\right)^{\frac{1}{2}} \]  \hspace{1cm} 6.14

where \(\varepsilon_0\) is the permittivity of free space, \(\kappa\) is the dielectric constant of InAs, \(k_0\) is Boltzmann’s constant, and \(T\) is the temperature. The bulk thickness is then estimated by

\[ d_b = d - d_s \]  \hspace{1cm} 6.15
6.5. Experimental Procedure

In what follows, a method of using this two-layer model to extract both the surface and bulk electrical properties of n-type InAs thin films directly from variable magnetic field Hall measurements is illustrated (Botha et. al., 2005; Krug et. al., 2007). Hall measurements were carried out on two undoped InAs films, 16 and 22 µm thick. The films, grown on 2°off (100) orientated GaAs substrates, were deposited at a growth temperature of 650 °C and a V/III of 10. Resistivity and Hall voltage were measured as a function of magnetic field for temperatures ranging from 13 K to room temperature. The zero field resistivity was recorded for each temperature.

Furthermore, the two-layer model will be used to simulate InAs Hall data with the aim of illustrating the short falls of conventional Hall measurements (Botha, Shamba and Botha, 2008). For the purpose of illustration, a Zn-doped series of InAs epitaxial layers was grown by atmospheric MOCVD (Chapter 3) with the aim of obtaining p-type material. These layers (~7 µm in thickness) were deposited on SI undoped GaAs substrates, at a growth temperature of 600 °C and a V/III of 5, with the precursor mole fractions given by [TBAs] = 3.4×10⁻⁴, [TMIn] = 6.8×10⁻⁵, and [DMZn] = 0, 1.7×10⁻⁷, 6.8×10⁻⁷, 1.4×10⁻⁶, and 5.5×10⁻⁶ for the respective layers. An additional series (~5 µm in thickness), in which the [DMZn] was kept constant at 4.3×10⁻⁶ and the V/III was varied from 5 to 40, was also grown. This V/III series was grown on both (100) and 2°off (100) orientated GaAs substrate. Room temperature Hall measurements were performed on all layers, with a magnetic field strength of 1 kG.

6.6. Extracting Hall Data

Using the two-layer model, the following method is used to extract surface and bulk electrical properties of unintentionally-doped n-type InAs thin films directly from variable magnetic field Hall measurements. For a given InAs thin film, the zero B-field conductivity together with the dependence of the Hall coefficient and magnetoresistivity
on magnetic field strength are measurable quantities. The sample thickness can also be measured, and \( e, \varepsilon_0, \kappa, \) and \( k_0 \) are known constants. The bulk layer thickness can be expressed in terms of \( d \) and \( d_s \) according to equation 6.15, and from equation 6.14 it is seen that \( d_s \propto n_b^{-1/2} \) (assuming \( n_b = n >> p \)). Thus, there are essentially four unknowns \( (\mu_b, n_b, \mu_s \) and \( n_s) \) in three equations (equations 6.5, 6.6, and 6.7), and the problem is underdetermined.

To overcome this setback, the following method is employed: Equations 6.5, 6.6 and 6.7 are reduced to equations 6.16, 6.17 and 6.18 by substituting equations 6.19 – 6.23 into equations 6.5, 6.6 and 6.7.

\[
R_H = \frac{d \left[ \beta + k \theta B^2 \right]}{\left[ \alpha + \theta^2 B^2 \right]} \tag{6.16}
\]

\[
\frac{\Delta \rho}{\rho_0} = \frac{\gamma B^2}{\left[ \alpha + \theta^2 B^2 \right]} \tag{6.17}
\]

\[
\sigma_0 = \frac{\sqrt{\alpha}}{d} \tag{6.18}
\]

where

\[
\alpha = (\mu_b n_b e d_b + \mu_s n_s e d_s)^2 \tag{6.19}
\]
Values for $\alpha$, $\beta$, $\theta$, $\gamma$ and $k$ are then obtained. By inverting equation 6.17, the following straight line equation is obtained:

$$\frac{\rho_0}{\Delta \rho} = \frac{\alpha}{\gamma} B^2 + \frac{\theta^2}{\gamma}$$

with gradient $m = \alpha/\gamma$ and y-intercept $c = \theta^2/\gamma$ which can be determined from a plot of $\rho_0/\Delta \rho$ vs $B^2$ (Figure 6.2 a). As seen in equation 6.18, $\alpha$ can be expressed in terms of measurable quantities. Thus, $\gamma = \alpha/m$ and $\theta = (c/\gamma)^{1/2}$ can also be expressed in terms of measurable quantities. To obtain $\beta$ and $k$, equation 6.16 is employed. $R_H$ vs $B$ is plotted, and while fixing $d$, $\alpha$, and $\theta$; $\beta$ and $k$ are allowed to vary until a curve that best fit $R_H$ vs $B$ is obtained (Figure 6.2 b). Once $\alpha$, $\beta$, $\theta$, $\gamma$ and $k$ are known the problem can be restated as five equations (equations 6.19 - 6.23) in four unknowns, and $\mu_b$, $n_b$, $\mu_s$ and $n_s$ can be obtained by solving any four of the five equations simultaneously.

Here, equations 6.19, 6.20, 6.21 and 6.23 are used in the electrical characterization of the 16 and 22 $\mu$m InAs samples. Figure 6.3 and Figure 6.4 show, respectively, the carrier concentration and mobility of both the 16 and 22 $\mu$m samples as a function of temperature. In Figure 6.3a and Figure 6.4a, the conventional Hall equations were used to determine carrier concentration and mobility, while Figure 6.3b and Figure 6.4b show the results of the two-layer model. The latter shows that the carrier concentration of the bulk is lower than that of the surface layer, while the mobility of the surface layer is lower than that of the bulk material. This finding is in agreement with literature (Watkins et. al.,
1995), and the shielding by the surface layer of the InAs bulk properties when using the conventional Hall equations is clearly seen by observing the thickness dependence of Hall data in Figure 6.3a and Figure 6.4a. For the thinner layer, the surface properties are more dominant, and the carrier concentration of the 16 µm layer appears higher than that of the 22 µm layer, while the mobility of the 16 µm layer appears lower than that of the 22 µm layer. The bulk carrier concentration in Figure 6.3b is far closer to the intrinsic carrier concentration than it is in Figure 6.3a, indicating that the samples are purer than conventional Hall analysis would imply. The temperature dependence of mobility due to polar optical mode scattering approaches $\mu \propto T^{-1/2}$ at high temperatures (Wiley, 1975). This $T^{-1/2}$ temperature dependence of mobility is observed in Figure 6.4b for bulk InAs, and indicates that polar optical mode scattering may dominate at high temperatures.
Hall measurements carried out by Wang et al (Wang et. al., 1992) were used to test the validity of the proposed method. Wang and coworkers used cyclotron resonance measurements to determine $\mu_b$, $n_b$, and $\mu_s$ of a 2.4 $\mu$m InAs film grown on GaAs by MBE, and the Shubnikov-de Haas effect was used to determine the concentration of the surface charge accumulation in this layer. Here, the two-layer model was used to analyse Hall data (77 K) taken by Wang et. al.. The agreement of these results with those obtained by this group is shown in Table 6.1. In this case, all five of the possible equation combinations used to simultaneously solve for $\mu_b$, $n_b$, $\mu_s$, and $n_s$, were used, and it is the average of these values that is given in Table 6.1. Table 6.2 shows the variation of results with choice of equation combination. By way of procedure, $\alpha$, $\beta$, $\theta$, $\gamma$ and $k$ have varying degrees of accuracy, and hence accuracy will vary with equation combination. Since $\sigma_0$ was not given by Wang et. al., it was estimated with the aid of equation 6.7 and the measured values for mobility and carrier concentration given by this group. This, together with the error introduced by reading the Hall data off a graph given in Wang et. al. are contributing factors to the relatively large variation in results. In an attempt to minimize the variation in results, $\theta$ was also allowed to vary with $\beta$ and $k$ in the final fitting step, and it is these results that are given in Table 6.1 and Table 6.2.

Table 6.1: Results of a two-layer analysis of Hall data (77 K) taken from Wang et al for a 2.4 $\mu$m InAs layer grown on GaAs by MBE. These results are compared to those obtained by Wang et al by other means viz. cyclotron resonance ($\mu_b$, $\mu_s$, $n_b$) and Shubnikov-de Haas measurements ($n_s$).

<table>
<thead>
<tr>
<th></th>
<th>$n_s$ (cm$^{-3}$)</th>
<th>$n_b$ (cm$^{-3}$)</th>
<th>$\mu_s$ (cm$^2$/Vs)</th>
<th>$\mu_b$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-Layer Model</td>
<td>$4 \times 10^{16}$</td>
<td>$4 \times 10^{13}$</td>
<td>$2 \times 10^4$</td>
<td>$2 \times 10^5$</td>
</tr>
<tr>
<td>Wang et al</td>
<td>$6 \times 10^{16}$</td>
<td>$2 \times 10^{14}$</td>
<td>$2 \times 10^4$</td>
<td>$2 \times 10^5$</td>
</tr>
</tbody>
</table>

Table 6.2: Variation of results with choice of combination of $\alpha$, $\beta$, $\theta$, $\gamma$, and $k$.

<table>
<thead>
<tr>
<th>Combination</th>
<th>Mean</th>
<th>Std Dev</th>
<th>% Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha\beta\gamma\theta\gamma$</td>
<td>$1.8 \times 10^5$</td>
<td>$1.7 \times 10^3$</td>
<td>$2.3 \times 10^3$</td>
</tr>
<tr>
<td>$\alpha\beta\theta\gamma$</td>
<td>$1.5 \times 10^4$</td>
<td>$2.6 \times 10^4$</td>
<td>$1.8 \times 10^4$</td>
</tr>
<tr>
<td>$\alpha\theta\gamma\theta\gamma$</td>
<td>$5.8 \times 10^{13}$</td>
<td>$1.6 \times 10^{13}$</td>
<td>$2.5 \times 10^{13}$</td>
</tr>
<tr>
<td>$\beta\gamma\theta\gamma$</td>
<td>$6.5 \times 10^{16}$</td>
<td>$2.1 \times 10^{16}$</td>
<td>$3.5 \times 10^{16}$</td>
</tr>
</tbody>
</table>
6.7. Simulating Hall Data

In this section, Equations 6.5 and 6.6 are used to simulate room temperature Hall coefficient and conductivity data for a two-layer InAs system. Equations 6.2 and 6.3 are then used to predict the apparent carrier concentration and mobility that will be determined from conventional Hall measurements, with the aim of illustrating the error of such a simplified analysis. The parameters used in the simulation of InAs Hall data are given in Table 6.3. These parameters were fixed in the execution of the above simulations, while \( n \) was made to vary from \( 1 \times 10^{11} \) to \( 1 \times 10^{18} \) cm\(^{-3} \). The hole concentration was then determined from

\[
p = \frac{n^2}{n}
\]

Table 6.3: Parameters used in the simulation of Hall data for InAs at room temperature (300 K).

<table>
<thead>
<tr>
<th>Variable/Constant</th>
<th>Value</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intrinsic Carrier Concentration ( (n_i) )</td>
<td>( 1 \times 10^{15} )</td>
<td>cm(^{-3} )</td>
<td>Wieder, 1974</td>
</tr>
<tr>
<td>Dielectric Constant ( (\kappa) )</td>
<td>14.6</td>
<td>-</td>
<td>Sze, 1981</td>
</tr>
<tr>
<td>Bulk Mobility ( (\mu_n) )</td>
<td>( 3.3 \times 10^4 )</td>
<td>cm(^2)/V.s</td>
<td>Schroder, 1998</td>
</tr>
<tr>
<td>Bulk Mobility Ratio ( (b) )</td>
<td>71.7</td>
<td>-</td>
<td>Schroder, 1998</td>
</tr>
<tr>
<td>Surface Mobility ( (\mu_s) )</td>
<td>( 5.3 \times 10^3 )</td>
<td>cm(^2)/V.s</td>
<td>Taken from the two-layer model analysis of n-type InAs</td>
</tr>
<tr>
<td>Surface Carrier Density ( (n_s) )</td>
<td>( 4.1 \times 10^{12} )</td>
<td>cm(^{-2} )</td>
<td></td>
</tr>
<tr>
<td>Magnetic Field Strength ( (B) )</td>
<td>0.1</td>
<td>T</td>
<td></td>
</tr>
</tbody>
</table>

Simulated results for the apparent carrier concentration and mobility (obtained from conventional Hall approximations) are shown as a function of the true hole concentration in Figure 6.5. The thickness dependence of conventional Hall measurements, as a result of surface charge accumulation, is also illustrated in these figures. To simulate the behaviour of bulk material, the surface accumulation layer was ignored, and equation 6.12 alone was used to simulate the Hall coefficient. Clearly, for bulk material, the
Figure 6.5: Simulation of apparent carrier concentration and mobility as a function of true hole concentration for various layer thicknesses. In the case of carrier concentration, dotted lines indicate n-type carriers, while solid lines indicate p-type carriers.
approximation of equation 6.2 is invalid in the region $2 \times 10^{15} < p < 2 \times 10^{17}$ cm$^{-3}$, where an erroneous jump from strongly n-type to strongly p-type material is predicted. This singularity results when the simulated Hall coefficient (equation 6.12) equals zero, and the use of equations 6.2 and 6.3 result in an asymptote in carrier concentration and mobility being observed at

$$p = \sqrt{\left(\mu_n^2 B^2 + b^2\right) n_i^2}$$

When surface effects are included, the shielding of hole conduction increases even further. To test the validity of these simulations, the measured carrier concentration, using conventional Hall measurements, of the Zn-doped InAs series (Figure 6.6) and the V/III InAs series (Figure 6.7) was compared to the simulated apparent carrier concentration curves, for the appropriate layer thicknesses, to estimate the true hole concentration in the respective layers. The measured mobility of the grown layers was then plotted against the estimated true hole concentration. The results show that the measured mobility does obey the simulated trend. Also, increasing [DMZn] by a factor of 32, yields a corresponding increase in the true hole concentration by a factor of ~ 45. This positive correlation between [DMZn] and the true hole concentration further supports the accuracy of the simulated Hall data. The error bars in Figure 6.7 indicate an uncertainty in the true hole concentration of the InAs layers grown with higher V/III ratios. The measured carrier concentration of these layers fall below the simulated curve, and can thus not be placed on the curve in order to extrapolate true hole concentration values.

It is pointed out that because of surface shielding effects, and the high mobility ratio of InAs, InAs layers that might be considered n-type by conventional Hall characterization may in fact be p-type material. This inaccuracy can lead to problems in device fabrication, where carrier type and concentration are critical to the properties and performance of devices.
Figure 6.6: Comparison of the measured Hall data of the Zn-doped InAs series with simulated Hall data. In the case of carrier concentration, dotted lines indicate n-type carriers, while solid lines indicate p-type carriers.
Figure 6.7: Comparison of the measured Hall data with the simulated Hall data for the V/III InAs series. In the case of carrier concentration, dotted lines indicate n-type carriers, while solid lines indicate p-type carriers. Similarly, open symbols indicate n-type layers, while solid symbols indicate p-type material. Here, circles indicate layers grown on 100 orientated substrate, while triangles indicate 2º off (100) substrate.
6.8. Concluding Remarks

In this chapter the short falls of conventional Hall measurements with respect to the electrical characterization of InAs thin films have been pointed out, and a more accurate method of extracting the electrical properties of n-type InAs from Hall data has been illustrated. For p-type InAs, the situation is complicated by the relatively large electron to hole mobility ratio of InAs which tends to conceal the p-type nature of InAs thin films from Hall measurements. This effect was illustrated by theoretically simulating InAs Hall data for both n- and p-type InAs. It is pointed out that because of surface shielding effects, and the high mobility ratio of InAs, InAs layers that might be considered to be n-type by conventional Hall characterization may in fact be p-type material.
Chapter 7: Concluding Remarks

This study focused on two aspects of the development of InAs/GaInSb SLS’s by MOCVD viz. the deposition of nano-scale (\(< 100 \text{ Å}\)) GaInSb layers, and the electrical characterization of unstrained InAs.

The first part of this study (Chapter 5) aimed to study the MOCVD growth of GaInSb layers in terms of deposition rate, growth mode, and indium incorporation on the nano-scale. Due to the limitations of conventional TEM and XRD in relation to resolution and sensitivity, the structural characterization of a single nano-scale epitaxial layer cannot be determined. For this reason, GaInSb layers were grown as part of a GaInSb/GaSb quantum well (QW) structure. By using this approach, the GaInSb QW’s (\(< 100 \text{ Å}\)) could be characterized with the use of photoluminescence spectroscopy, which, when used in conjunction with TEM and/or XRD, proves useful in the analysis of such small scale deposition. Based on the growth rates and In content of GaSb and GaInSb calibration layers, two QW structures, S1 and S2, were grown with a nominal In content of 12.7 % and 20.4 %, respectively. Each structure consisted of four QW’s of different thicknesses, and was simultaneously grown on both (100) and 2° off (100) GaSb(Te) substrates. The aim of this study was to firstly observe the nano-scale growth of GaInSb in terms of growth rate and In incorporation. Secondly, a comparison of substrate orientation was made, with the aim of determining the preferred substrate orientation for QW deposition. The results show that the resulting growth rates of the GaInSb nano-layers approaches the nominal growth rates determined from GaInSb calibration layers. The In incorporation efficiency in nano-layers, however, was markedly lower than what was predicted by the GaInSb calibration layers. This observed decrease in indium incorporation could be related to the effects of strain on the In incorporation of strained nano-layers. Regarding the choice of substrate orientation for QW deposition, it appears that growth on non-vicinal substrates is more conducive to the deposition of high quality QW structures.
The MOCVD growth of InAs is simplified by the binary nature of the compound and the high vapour pressure of arsine at typical growth temperatures. The former eliminates the need for alloy composition studies, while the latter significantly increases the range of \( V/III \) ratios that result in good solid stoichiometry and allows for a wide range of favorable InAs growth parameters. For this reason, the deposition of InAs on the nanoscale was not considered in this study.

What was of interest in this study is the electrical characterization of InAs thin films, and this formed the basis of the second part of this work (Chapter 6). It is long known that conventional Hall measurements cannot be used to accurately characterize InAs epitaxial layers, as a result of parallel conduction resulting from surface and/or interface effects. Knowledge of the true electrical properties of InAs is essential in the design of SLS devices. This study looked at extracting the surface and bulk electrical properties of n-type InAs thin films directly from variable magnetic field Hall measurements. This was done by treating an InAs layer as a two-layer system consisting of a bulk and a surface layer, and employing the two layer model of Nedoluha and Koch (Nedoluha, A. and Koch, K. M. (1952) Zeitschrift für Physik 132, 608). In agreement with literature, the results showed that the carrier concentration of the bulk is lower than that of the surface layer, while the mobility of the surface layer is lower than that of the bulk material. For p-type InAs, the situation is complicated by the relatively large electron to hole mobility ratio of InAs which tends to conceal the p-type nature of InAs thin films from Hall measurements. Here, this effect was illustrated by way of theoretical simulation of Hall data.

It was pointed out that because of surface shielding effects, and the high mobility ratio of InAs, InAs layers that might be considered n-type by conventional Hall characterization may in fact be p-type material. This inaccuracy can lead to problems in device fabrication, where carrier type and concentration are critical to the properties and performance of devices.
References


Vankova, V. (2002) The Development of Metalorganic Vapour Phase Epitaxial GaInSb, GaAsSb and GaInAsSb - Dissertation


Appendix A : Material Properties

The material parameters required in Chapter 5 are listed in Table A.1 and Table A.2. Unless otherwise stated, the information presented in this appendix has been taken from the work of Vurgaftman et. al. (Vurgaftman, Meyer and Ram-Moham, 2001).

The band parameters of Ga$_{1-x}$In$_x$Sb are determined from the band parameters of the constituent binaries by way of quadratic interpolation. If $P$ is any band parameter then

$$P_{GaInSb} = (1-x)P_{GaSb} + xP_{InSb} - x(1-x)C$$ \hspace{1cm} \text{A.1}

Here, $C$ is known as the bowing parameter and accounts for the deviation (if any) from a linear interpolation between the two binaries.

Bandgap

The zero kelvin $\Gamma$-point bandgap energies for the binary compounds GaSb and InSb are listed in Table A.1. To obtain the bandgap as a function of temperature ($T$), the Varshni expression is employed, where $\alpha$ and $\beta$ are known as the Varshni parameters.

**Varshni expression:**

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$ \hspace{1cm} \text{A.2}

The expression for calculating the bandgap of Ga$_{1-x}$In$_x$Sb given by Madelung (Madelung, 1996) differs from that obtained from Vurgaftman et. al. in that Madelung takes the temperature dependence of the bandgap bowing parameter into account, while Vurgaftman et. al. do not. The bandgap expression provided by Madelung has been used in this work, and is given below.
Madelung:  
\[ E_g(x,T) = E_g(x,0) - \frac{\alpha_1 T^2 (1-x)}{\beta_1 + T} - \frac{\alpha_2 T^2 (x)}{\beta_2 + T} + x(1-x)C_T T \]  \hspace{1cm} A.3

Where
\[ \alpha_1 = 0.62meV/K \]
\[ \alpha_2 = 0.38meV/K \]
\[ \beta_1 = 260K \]
\[ \beta_2 = 200K \]
\[ C_T = 0.05meV/K \]

**Effective Mass**

The expressions used to determine the electron and heavy-hole effective masses are given below.

Electron:  
\[ \frac{m_0}{m_e} = (1 + 2F) + \frac{E_p \left( E_g + \frac{2}{3} \Delta_{SO} \right)}{E_F \left( E_g + \Delta_{SO} \right)} \]  \hspace{1cm} A.4

Heavy-hole:  
\[ \frac{m_0}{m_{hh}} = \gamma_1 - 2\gamma_2 \]  \hspace{1cm} A.5

**Lattice Constant**

In addition to the lattice constants of GaSb and InSb, the lattice constants of GaAs and InAs are also required (section 5.1.2), and these are given in Table A.2.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Lattice constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>5.65325</td>
</tr>
<tr>
<td>InAs</td>
<td>6.0583</td>
</tr>
<tr>
<td>Parameter</td>
<td>Symbol</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero kelvin bandgap</td>
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<tr>
<td>Varshni parameters</td>
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<tr>
<td></td>
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<tr>
<td>Spin-orbit splitting</td>
<td>Δ₆⁵₆</td>
</tr>
<tr>
<td>Luttinger parameters</td>
<td>γ₁</td>
</tr>
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<td></td>
<td>γ₂</td>
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<td>Interband matrix element</td>
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<tr>
<td>Kane parameter</td>
<td>F</td>
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<tr>
<td>Valence band offset w.r.t. GaSb</td>
<td>VBO</td>
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<tr>
<td>Hydrostatic deformation potential</td>
<td>aₐ</td>
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<td></td>
<td>aₐ</td>
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<tr>
<td>Shear deformation potential</td>
<td>b</td>
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<tr>
<td>Elastic constants</td>
<td>C₁₁</td>
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<td></td>
<td>C₁₂</td>
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</table>
Appendix B : Publications

During the course of this study, the following manuscripts were accepted for publication:

Botha, J. R., Vankova, V., Botha, L., and Gladkov, P.
“Influence of growth conditions on the optical and electrical properties of MOVPE-grown InAs$_{1-x}$Sb$_x$”

“Electrical properties of undoped and doped MOVPE-grown InAsSb”

Botha, L., Shamba, P., and Botha, J. R.
“Electrical characterization of InAs thin films”
Physica Status Solidi (c) 5, 620 (2008)

The following presentations were made at national and international conferences:

Botha, J. R., Vankova, V., Botha, L., and Gladkov, P.
“Influence of growth conditions on the optical and electrical properties of MOVPE-grown InAs$_{1-x}$Sb$_x$”
Poster presentation at the 12th International Conference on Narrow Gap Semiconductors, Toulouse, France (July, 2005)
Botha, L., and Botha, J. R.
“Electrical Characterization of InAs: Bulk Versus Surface Properties”.
Poster presentation at the 50th Annual Conference of the South African Institute of
Physics, Pretoria, South Africa (July, 2005)

Botha, L., Krug, T., Berndt, P. R., Neethling, J. H., and Botha, J. R.
“Metalorganic chemical vapour deposition of InAs/GaInSb superlattices for application
in far infrared detection.”
Poster presentation at the 51st Annual Conference of the South African Institute of
Physics, Cape Town, South Africa (July, 2006)

Botha, L., and Botha, J. R.
“Electrical Characterization of InAs: Bulk Versus Surface Properties.”
Essay presentation at the 51st Annual Conference of the South African Institute of
Physics, Cape Town, South Africa (July, 2006)

Botha, J. R.
"Electrical properties of undoped and doped MOVPE-grown InAsSb“
Poster presentation at the International Conference on MOVPE, Miyazaki, Japan (May
2006)

Botha, L., Krug, T., Neethling, J. H., and Botha, J. R.
“Growth of GaInSb epitaxial layers on (001) GaSb substrates”
Oral presentation at the 45th Conference of the Microscopy Society of Southern Africa,
Port Elizabeth, South Africa (November/December, 2006)
Botha, L., Shamba, P., and Botha, J. R.

“Electrical characterization of InAs thin films”

Oral presentation at the Conference on Photonic Materials, Kariega Game Reserve, Eastern Cape, South Africa (May, 2007)