Development of InSb/GaSb quantum dots by MOVPE

Chinedu Christian Ahia

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Change the World

Development of InSb/GaSb quantum dots by MOVPE

By

Chinedu Christian Ahia

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Promoter: Professor J. R. Botha

Dedication

To my parents

"Observe people who are good at their work – skilled workers are always in demand and admired; they don't take a backseat to anyone"

Proverbs 22:29 (MSG)

NELSON MANDELA

UNIVERSITY

DECLARATION BY CANDIDATE

NAME:	Chinedu Christian AHIA	-
STUDENT NUMBER:	213508826	•
QUALIFICATION:	PhD	-
TITLE OF PROJECT:	Development of InSb/GaSb quantum dots by MOVPE	

DECLARATION:

In accordance with Rule G5.6.3, I hereby declare that the above-mentioned treatise/dissertation/thesis is my own work and that it has not previously been submitted for assessment to another University or for another qualification.

SIGNATURE:

DATE: _____ 27/08/2018

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Research outputs

National and International Conference Presentations

<u>C. C. Ahia</u>, J. R. Botha, N. Tile, E. J. Olivier, "*Photoluminescence and structural properties of single and double MOVPE-grown InGaSb/GaSb quantum wells*". Poster presentation at the 7th South African Conference on Photonic Materials (SACPM 2017) workshop held in Amanzi Private Game Reserve, South Africa (*27-31* March *2017*).

<u>C. C. Ahia</u>, J. R. Botha, N. Tile, E. J. Olivier, *"Near-infrared photoluminescence study of stacking effect and mole fraction on InSb/GaSb quantum dot structures"*. Poster presentation at the 4th Conference on Sensors, MEMS and Electro-Optical Systems (SMEOS 2016) workshop held in Kruger Park, South Africa (*12-14* September *2016*).

<u>C. C. Ahia</u>, N. Tile, Z. N. Urgessa, J. R. Botha, J. H. Neethling, *"An investigation of near-infrared photoluminescence from AP-MOVPE grown InSb/GaSb quantum dot structures"*. Poster presentation at the 18th International Conference on Metal Organic Vapor Phase Epitaxy (ICMOVPE 2016) workshop held in San Diego, California, USA (*10-15* July *2016*).

<u>C. C. Ahia</u>, Z. N. Urgessa, J. R. Botha, *"An investigation of near-infrared photoluminescence from AP-MOVPE grown InSb/GaSb quantum dot structures"*. Oral presentation at the National Laser Center (NLC) Rental Pool Programme report meeting held in the Stellenbosch Institute for Advanced Study (STIAS) South Africa (15-17 November 2016).

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Conference of the South African Institute of Physics (SAIP 2015) workshop held in Port Elizabeth, South Africa (*29*th June-*03* July *2015*).

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Publications

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<u>Chinedu Christian Ahia</u>, Ngcali Tile, J. R. Botha, E. J. Olivier. "*Photoluminescence and structural properties of unintentional single and double InGaSb/GaSb quantum wells grown by MOVPE*". Physica B 535 (2018) 13-19, https://doi.org/10.1016/j.physb.2017.007

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Ngcali Tile, <u>Chinedu C Ahia</u>, Jaco Olivier, Johannes Reinhardt Botha. "*Atmospheric pressure-MOVPE growth of GaSb/GaAs quantum dots*". Physica B *535* (*2018*) *20-23*, https://doi.org/10.1016/j.physb.2017.06.014

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Abbreviations

0D	-	Zero dimensional
1D	-	One dimensional
2D	-	Two dimensional
3D	-	Three dimensional
AFM	-	Atomic force microscopy
Al	-	Aluminium
Sb	-	Antimony
BE4	-	Bound exciton
BF	-	Bright-field
CdSe	-	Cadmium selenide
CdS	-	Cadmium sulphide
СТЕМ	-	Conventional transmission electron microscopy
CVD	-	Chemical vapour deposition
DF	-	Dark-field
DOS	-	Density of states
DHE	-	Droplet hetero-epitaxial
m_h	-	Effective mass of holes
m _e	-	Effective mass of electrons
EDS	-	Energy-dispersive X-ray spectroscopy
FIR	-	Far-infrared
FM	-	Frank-Van der Merwe
FWHM	-	Full width at half maximum
Ga	-	Gallium
GaSb	-	Gallium antimonide
GaAs	-	Gallium arsenide

GPIB	-	General Purpose Interface Bus
HAADF	-	High angle annular dark field
НН	-	Heavy hole
HRTEM	-	High resolution transmission electron microscopy
In	-	Indium
IR	-	Infrared
InSb	-	Indium antimonide
InAs	-	Indium arsenide
InGaSb	-	Indium gallium antimonide
InP	-	Indium phosphide
Pb	-	Lead
PbS	-	Lead sulphide
LEDs	-	Light-emitting diodes
LPE	-	Liquid-Phase Epitaxy
LWIR	-	Long wavelength infrared
MFM	-	Magnetic Force Microscopy
MBE	-	Molecular Beam Epitaxy
MOCVD	-	Metalorganic chemical vapour deposition
MOVPE	-	Metalorganic Vapour Phase Epitaxy
<i>HgCdTe,</i> or <i>MCT</i>	-	Mercury cadmium telluride
MWIR	-	Medium wavelength infrared
MIR	-	Mid-infrared
ML	-	Monolayers
ML/s	-	Monolayer per second
NSOM	-	Near-Field Scanning Optical Microscopy
OMVPE	-	Organometallic vapour phase epitaxy
PL	-	Photoluminescence

PID	-	Proportional-integral-derivative
QCL	-	Quantum cascade lasers
QD	-	Quantum dot
QDs	-	Quantum dots
QW	-	Quantum well
QWs	-	Quantum wells
QWRs	-	Quantum wires
RHEED	-	Reflection high energy electron diffraction
RMS	-	Root mean square
SPM	-	Scanning probe microscopy
SEM	-	Scanning electron microscopy
STM	-	Scanning Tunnelling Microscopy
SK	-	Stranski-Krastanov
SLM	-	Standard litres per minute
TDMASb	-	Trisdimethylaminoantimony
ТЕМ	-	Transmission electron microscopy
TEGa	-	Triethylgallium
TEIn	-	Triethylindium
TESb	-	Triethylantimony
ТМGа	-	Trimethylgallium
TMIn	-	Trimethylindium
TMSb	-	Trimethylantimony
VW	-	Volmer-Weber
WL	-	Wetting layer
WD	-	Working distance
XRD	-	X-ray diffraction

Summary

There has been an increasing interest in the modification of semiconductor band structures through the reduction of their dimensions, which simultaneously increases the band gap energy of the material and gives rise to flexibility in device properties. Advances in III-V antimony (Sb) based semiconductor fabrication have triggered the quest for extension of the emission/absorption wavelength range of this family of compounds for optoelectronic devices operating in the mid-infrared region of the electromagnetic spectrum. An interesting material system for mid-infrared (MIR) applications is indium antimonide (InSb) quantum dots (QDs) within a gallium antimonide (GaSb) matrix. However, its band alignment and emission wavelength has been the subject of some interest and controversy over the years.

This study focuses on the development of InSb/GaSb QDs by metal organic vapour phase epitaxy (MOVPE). The samples were grown on different substrates using various growth parameters in order to vary the size, density and aspect ratio of the dots. Interfacial growth interruptions while flowing various source precursors through the reactor were investigated in order to influence the chemical termination of the surface, and hence the resulting strain in the structures. The samples were characterized using photoluminescence spectroscopy, scanning probe microscopy, scanning electron microscopy, X-ray diffraction and transmission electron microscopy. Likewise, the band alignment, energy levels, and carrier wave functions of the samples in this work were modelled theoretically using the nextnanomat software (version 3.1.0.0).

A comparison of growth on two different GaSb substrates [(100) 2° off towards <111>B \pm 0.1° and (111) \pm 0.1°] using similar growth conditions yielded a higher dot density on the (100) substrate compared to the (111) substrate. This was attributed to the presence of terraces/atomic steps induced by the misorientation on the (100) substrate, which invariably gives rise to increased adsorption and an enhanced sticking coefficient of adatoms. Studies on the influence of a buffer layer on the morphology of uncapped dots showed that the shape and size of the dots are sensitive to the thickness of the buffer layer. In some case a corrugated buffer surface resulted, which introduced order in the arrangement of the dots, which formed preferentially inside the troughs. An increase in the V/III ratio from 1.0 to 3.0 was found to reduce the areal density of the QDs, while an

analysis of the diameter histograms showed a narrowing of the size distribution with an increase in V/III ratio. The larger size distribution at low V/III was ascribed to the increase in indium species and the increased indium adatom migration length. This leads to increased dot density and nucleation sites, and thus triggers an increase in the conversion of tiny QDs into thermodynamically more suitable larger dots via coalescence. However, as the V/III ratio increased, the number of indium adatoms available for growth on the surface reduced, which automatically led to a decrease in the migration length of indium species which is unfavourable for the production of nucleation sites and to a decrease in dot density. Low growth rates were found to be beneficial for the growth of a high density (\sim 5×10¹⁰cm⁻²) of QDs.

Photoluminescence (PL) analysis of the capped samples at low temperature (~10 K), using an excitation power of 2 mW, showed a PL peak at ~732 meV. Upon an increase in laser power to 120 mW, a blue shift of ~ 8 meV was noticed. This emission typically persisted up to 60–70 K. An increase in the number of InSb QD-layers, was observed to cause an increase in the luminescence spectral line width and a long-wavelength shift of the PL lines, together with an enhancement in the strength of the PL emission. However, high resolution transmission electron microscopy (HRTEM) of the capped dots revealed the formation of an InGaSb quantum well-like structure, ~10 nm thick, which was responsible for the PL signal mentioned above. The absence of QDs in the capped sample was attributed to inter-diffusion of Ga and In during the deposition of the cap layer, giving rise to a quantum well (QW) instead of the intended QDs. The presence of threading dislocations and stacking faults were also observed in the TEM micrographs of the samples containing multilayers, which can account for the fast quenching of the PL emission with increasing temperature from these samples. Theoretical simulations of the band alignment, wave functions and energy levels were in good agreement with the data collected from the PL spectra of the samples.

Chapter 1 Introduction

The remarkable improvement in the fabrication of low dimensional semiconductor structures achieved over the past few years has enabled the development of optoelectronic devices with wide spread applications. The miniaturization of bulk materials from three dimensions to zero dimensions and the flexibility in fabrication of semiconductor nanostructures have distinguished semiconductor quantum dots as promising for use in photonics, quantum communication and computation, spintronics and various other device applications. Similarly, the successful reduction of three dimensional bulk materials to two dimensional quantum well (QW) structures that produce fascinating optical and electronic properties, have attracted the attention of researchers for several decades. Prompted by these stimulating outcomes, there have been intensified investigations to modify the properties of these semiconducting materials and further reduce their dimensions.

Quantum dots (QDs) are small regions in semiconductors where excitons are confined in three dimensions. Due to the effect of quantum confinement, QDs of various sizes but of similar materials can emit/detect different frequencies of light. Optical studies have demonstrated that the band gap of semiconductor QDs increases as their size decreases, which can be attributed to the quantum confinement potential. Despite much effort dedicated to the design of semiconductor QDs, it remains a challenge to fabricate a high quality coherent quantum dot (QD) that is free from defects. Some of these defects arise from the strain induced levels in the band gap of the dots, or from lattice mismatch between the dot material and the surrounding matrix.

Amongst the materials of interest III-V compound semiconductors have been studied widely. These consist of combinations of group III and V elements that form binary, ternary and quaternary compounds. The first III-V compound was reported in 1910 [1] when indium and phosphorous were synthesized. One of the advantages of III-V compounds is the ability to produce hetero-junctions epitaxially [2]. This involves the matching of the lattice parameters of each individual compound as closely as possible.

The lattice matching of these semiconductor compounds creates some complications, due to the unique lattice parameter of each compound. Figure 1.1 shows the energy gap of some semiconductor compounds at 300 K, including the III-V semiconductors, and their lattice constants.



Figure 1. 1. Lattice constants, band gap energies and corresponding wavelengths of III-V semiconductors at 300 K [3].

Antimony (Sb) is a lustrous grey semi-metal with atomic number 51 and an atomic weight of 121.760. It is a solid at room temperature and is mostly used in lead-acid batteries when alloyed with lead, increasing the durability of lead [4]. When combined with group III compounds such as gallium (Ga), indium (In) and aluminium (Al), it produces III-V binary compounds (GaSb, InSb and AlSb) which form the basis for more complex Sbbased ternary or quaternary compounds [4], useful for infrared (IR) detectors.

The development of infrared (IR) detector materials started after the discovery of IR radiation by William Herschel in 1800. These materials are basically used for image detection and measuring emission patterns of thermal heat radiation from objects. Energies from objects having temperatures between 0 and 1 000 °C are mostly emitted as radiation with IR wavelengths between 1 μ m and 20 μ m. The atmosphere has transmission windows in the 3 to 5 μ m medium wavelength infrared (MWIR) and 8 to

14 μ m long wavelength infrared (LWIR) regions [4]. These widows are evident in Figure 1.2, where the transmittance of the earth's atmosphere at sea level is plotted.



Figure 1.2. Infrared transmittance of the atmosphere at sea level [4].

The first functional IR detector was manufactured from lead sulphide (PbS) with a sensitivity to IR wavelengths of up to ~3 μ m [5]. The development of IR detector technology after World War II was predominantly propelled by military applications. Advances in IR detector technology were triggered by the discovery of HgCdTe (MCT) material system by Lawson and co-workers in 1959 [5]. MCT has been the leading material system for MWIR and LWIR photo-detectors, although it is characterised by instability and non-uniformity challenges over larger areas, resulting from the high Hg vapour pressure [4]. Because of this, the quest for a substitute IR material system has intensified over the years. Sb-based III-V semiconductors are widely studied as possible alternatives to MCT.

An interesting material system for mid-infrared (MIR) applications is the indium antimonide (InSb) QD within a gallium antimonide (GaSb) matrix. InSb can be used for very high speed electronic devices and for magneto-resistive sensors in the automotive industry [4]. InSb has a band gap energy of 0.18 eV at room temperature and a lattice mismatch of 6.3% compared to GaSb. InSb/GaSb QDs have a number of significant characteristics that distinguish them from any other QD system. The exciton confinement has been reported [6] to be stronger both laterally and along the growth direction compared to other QD systems. Techniques previously employed to synthesize these dots include Metalorganic Vapour Phase Epitaxy (MOVPE) [6] [7] [8], Molecular Beam Epitaxy (MBE) [9] [10], and Liquid-Phase Epitaxy (LPE) [11].

Prompted by the quest for alternative material systems for MIR application, this study will focus on the "Development of InSb/GaSb quantum dots by Metal-organic Vapour Phase Epitaxy". The outline of this thesis is as follows:

In Chapter 2, a summarized overview of QDs, their physical properties, applications, concepts of low dimensional systems and the role of lattice mismatch in the design of QDs, will be presented. Other topics that will be dealt with briefly in this chapter include the epitaxial growth mode leading to QD formation and a summarized review of critical layer thickness and its role in the formation of misfit dislocations. Similarly, an abridged literature review on the critical size of an island, and a survey of InSb and GaSb zincblende structures, as well as previous works on the epitaxial growth of InSb/GaSb QDs, will be presented.

Chapter 3 will focus on MOVPE growth techniques. The configuration of the MOVPE growth system will be discussed and a comparison will be made between MBE and MOVPE systems. Additional topics examined in Chapter 3 include a brief review of the advantages and challenges of the MOVPE growth technique. Growth parameters such as the V/III ratio, growth temperature and growth rate, reactor pressure, and substrate orientation will also be discussed.

Chapter 4 will focus mainly on the description of the experimental methods used or adopted during this study. Substrate preparation, precursor temperature and growth technique will be highlighted. Characterisation techniques used in this study, such as photoluminescence (PL) spectroscopy, scanning probe microscopy (SPM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and band structure simulation techniques, will also be examined. Details of the procedures ensured in determining the optimal growth conditions for InSb quantum dots, will be presented in Chapter 5. Likewise, the chemistry of all precursors used in this study, and the effect of the V/III ratio on the morphology and size distribution of QDs, will be highlighted in this chapter.

The effect of the GaSb substrate orientation and buffer layer on the growth of InSb QDs will be discussed in Chapter 6, while Chapter 7 will deal with the growth and PL characterisation of single layer InSb/GaSb QD structures. The properties and growth conditions of the samples will be discussed extensively in this chapter. Details of the SPM analysis of the uncapped samples, TEM and the PL analysis (excitation power dependent and temperature dependent measurements) of the capped samples will be presented. Furthermore, the effect of source mole fraction on the PL response of capped samples will be illustrated, while a detailed account of the technique adopted in extracting the apparent thermal activation energy for the samples and the band edge simulation will also be presented.

Chapter 8 will focus on the growth, structural and PL characterization of double layer InSb/GaSb QD structures. In this chapter, the effect of spacer layer thickness on the band edge emission and energy levels will be investigated via simulation technique using nextnanomat software.

The growth of stacked layers of InSb/GaSb quantum dot structures and their corresponding TEM and PL analysis will be presented in Chapter 9. Chapters 7 to 9 contains both bright-field (BF) and dark-field (DF) cross-sectional TEM micrographs of capped samples, as well as results from compositional analysis.

Finally, a summary of results and concluding remarks are presented in Chapter 10.

Chapter 2

Overview of quantum dots

2.1 Introduction

In 1932 [12], H.P. Rooksby found that the red or yellow colour from silicate glasses could be linked to microscopic inclusions of CdSe and CdS [13]. Only in 1985 these changes in colour were associated with the energy states governed by quantum confinement in either CdSe or CdS "quantum dots" [14]. The three-dimensional (3D) confinement of carriers in QDs induces localization of states for the valence and conduction band carriers, and discrete inter-band transition energies [15].

Quantum confinement can arise due to modification in the electronic and optical properties of a material with dimensions of the order of ~ 10 nm or less. This can induce electrons and holes to be compressed into a dimension described as the exciton Bohr radius. Strong confinement triggers a larger separation of energy levels and leads to a blue-shift of the emission/absorption onset as the size of the dots decreases. Conversely, a weaker confinement gives rise to a red-shift in the emission/absorption. The confinement effect leads to a collapse of the quasi-continuous energy bands of a bulk material into discrete, atomic-like energy levels [16], and an increase in recombination energy with decreasing QD size [17]. Hence the eigen energies increase for smaller QD sizes.

The first model calculation of electronic states of semiconductor crystallites small enough (~50 Å diameter) that the electronic properties differ from those of bulk materials was given by Louis Brus [18] [19]. According to this model, the energy of the lowest excited state can be expressed as:

$$E \simeq E_g + \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon R} + \frac{e^2}{R} \sum_{n=1}^{\infty} \alpha_n \left(\frac{S}{R} \right)^{2n} , \qquad (1)$$

where E_g is the band gap energy of the semiconductor, \hbar is the reduced Planck constant, m_e and m_h are the effective mass of electrons and holes, respectively, R is the radius of the QD, *e* is the electronic charge, ϵ is the dielectric constant and S is the single positional term. The second and third terms in equation (1) represent the kinetic and Coulomb energy terms, while the fourth term is the polarization energy term, which is very small. The bar over the fourth term signifies the average over a wave function Ψ . For a good understanding of the lowest-energy excitonic state, the polarization energy, which is the fourth term in equation (1), can be omitted [20]. In large band gap materials (where R \approx 85 Å,) the Coulomb term is important, while in small band gap materials this term is significantly smaller [19]. Using basic quantum mechanical principles, Brus's model provides an excellent understanding of the behaviour of the lowest-energy excitons [20]. The best distinct confirmation of quantum confinement in semiconductor nanocrystals is the shift in the optical absorption and emission spectra with size [20].

Despite being solid crystals consisting of materials identical to a conventional bulk-like structure, QDs function more like detached atoms and have unique characteristics which make them significantly different from the bulk material [21]. They are often made by colloidal synthesis involving a system of precursors and solvents that are mixed at a temperature dictated by the characteristics of the semiconductor nanocrystal that the mixture is designed to produce.

Epitaxial QDs are typically produced either by self-assembly or lithographic methods. Self-assembly, which is often referred to as a "bottom-up" approach, involves the spontaneous epitaxial growth of self-assembled dot islands resulting from a lattice mismatch between the dot and the substrate material. In self-assembled QDs, strong confinement is usually found in the growth direction and weaker confinement in the wetting layer (WL) plane [15]. The lithographic technique, or "top-down" approach, requires the application of a photo-sensitive material, known as a photo-resist, to the surface by spinning. The photo-resist is then baked and exposed to a pattern of intense light which produces a chemical change and permits certain regions (which later serve as sites for epitaxial growth/deposition) of the photo-resist to be removed in a liquid solution known as the "developer" [22]. An epitaxial film is deposited on top of the patterned photo-resist and wafer, and the photo-resist is removed afterwards via a process known as "lift-off".

QDs are promising and have a variety of applications in science and technology, most importantly in the field of medicine and biological sciences. Some of the opto-electronic applications include lasers, quantum computing, photovoltaic devices, amplifiers, light emitting diodes and photodetectors.

2.2 Concepts of low dimensional systems

The number of degrees of freedom of the electron (or hole) momentum in a bulk threedimensional (3D) semiconductor can be reduced to two dimensional (2D) quantum wells (QWs), one dimensional (1D) quantum wires (QWRs) and further to zero dimensional (0D) QDs. A reduction in the dimension of a semiconducting material gives rise to striking changes in the behaviour of these materials due to the confinement of electrons and holes. A particle in a finite well is an ideal representation of a quantum mechanically confined system. In such systems, the energy levels depend on the depth of the well, and tunnelling of the particle is often possible.



Figure 2. 1. Schematic geometry of spatial confinement in semiconductor materials and their corresponding electronic densities of states [17].

The schematic diagram in Figure 2.1 represents the change of the density of states (DOS) of semiconductor materials as a function of energy for each reduction in dimension. According to Figure 2.1, an increase in the DOS as the energy separation from the band edges increases is noticed for the bulk semiconductor. The carrier motion is not quantized and hence carriers are free to move in all three dimensions of space. As the semiconductor material is reduced from the 3D bulk structure to a 2D QW, the DOS is

seen to behave like a step function and the possible energies of carriers are only quantized in one direction. This implies that the QWs have two degrees of freedom (carriers can only move in two dimensions). A further reduction from a 2D QW to a 1D QWR leads to energy quantization in two directions; carriers are confined in two dimensions and are move in one dimension only (one degree of freedom). When carriers are confined in all three dimensions in a QD (i.e. the carriers have zero degrees of freedom of motion), the DOS becomes delta (δ)—like (analogous to those in an atom).

2.3 Lattice mismatch

The process of fabricating a semiconductor crystal material through the deposition of atoms in crystalline layers on a substrate, usually inside a high temperature chamber, is referred to as epitaxial growth. Homo-epitaxial growth occurs when a single crystal material is deposited on a substrate of the same material, while hetero-epitaxial growth occurs when a single crystal material is deposited on a different substrate. Hetero-epitaxial growth is usually characterised by strain, lattice mismatch and dislocations, which can influence the device performance of the semiconductor material. Lattice mismatch is a condition which occurs when two materials with different lattice constants are combined by depositing one material on top of the other. Large, built-in strain resulting from lattice mismatch has been identified as one of the difficulties linked with a hetero-epitaxial system [23]. The following equation can be used to describe the lattice mismatch between a substrate and epilayer:

$$\lambda = \frac{\mu_e - \mu_s}{\mu_s} , \qquad (2)$$

where λ represents the lattice mismatch, μ_e represents the lattice constant of the epilayer, and μ_s is the lattice constant of the substrate.

In lattice-matched growth, the epilayer and the substrate have identical lattice constants. Matched lattices are vital for various applications and are known to minimise defects and increase the mobility of carriers.



Figure 2. 2. Strained and relaxed hetero-epitaxial growth.

Normally, lattice mismatch prevents the growth of defect-free epitaxial materials. Figure 2.2(a) and (b) are schematic representations of a coherently strained epilayer formed by hetero-epitaxy. In Figure 2.2(a) the epilayer is stretched with reference to the substrate, thus shrinking the perpendicular lattice constant. This gives rise to tensile strain, where $\lambda < 0$. Likewise, in Figure 2.2(b), the lattice constant of the epilayer parallel to the interface is reduced so as to match that of the substrate, thereby forcing the lattice constant of the epilayer perpendicular to the interface to expand. This situation yields compressive strain, and $\lambda > 0$. Figure 2.2(c) shows the formation of lattice defects resulting from the relaxation which occurs when the growth of the epilayer exceeds a critical thickness.

2.4 Epitaxial growth modes and quantum dot formation

The application of epitaxial growth techniques as a method of choice for the fabrication of high quality semiconductor nanostructures has been well established over the years by different researchers. Apart from the MBE and MOVPE techniques, which are predominantly used for the development of QDs, other methods used to synthesize QDs include hydrothermal growth processes and microwave-assisted growth processes. The evolution of epitaxial material on a crystalline surface usually involves three possible growth modes. These are briefly summarized below.

2.4.1 Volmer-Weber growth mode

The Volmer-Weber (VW) growth mode involves the formation of 3D islands without the complete formation of a 2D wetting layer (WL). Hence, the incomplete wetting of the substrate by the epitaxially deposited material is energetically favourable. For the VW growth, the sum of the epilayer surface free energy and the interface free energy is greater than the substrate surface free energy. The formation of 3D islands by the adsorbate rather than a complete layer, indicates that the interfaces associated with the thin film has a higher interfacial free energy than the bare substrate, which causes the deposited atoms/molecules to be more strongly attached to each other than to the substrate.



Figure 2. 3. Volmer-Weber growth.

2.4.2 Frank-Van der Merwe growth mode

The Frank-Van der Merwe (FM) growth mode is a layer-by-layer (i.e. 2D) growth mode, corresponding to the complete wetting of the substrate by the deposited material. FM growth usually occurs when the sum of the epilayer and interface free energy is less than the substrate free energy. The adsorbate is characterised by the formation of a complete monolayer followed by the deposition of a second layer on it. This implies that the atoms of the deposited material are more strongly bound to the substrate than they are to each other. This mode is often inherent for material systems with insignificant or no lattice mismatch.



Figure 2. 4. Frank-Van der Merwe growth.

2.4.3 Stranski-Krastanov growth mode

The Stranski-Krastanov (SK) growth mode was named after Ivan Stranski and Lyubomir Krastanov [24]. This mode is normally characterized by the formation of a 2D layer, known as the wetting layer, followed by 3D islanding which occurs beyond a certain critical thickness of the wetting layer. The SK growth mode is a combination of both VW growth and FM growth and often arises in material systems with sufficient lattice mismatch.



Figure 2. 5. Stranski-Krastanov growth.

2.5 Review of critical thickness and its role in the formation of misfit

dislocations

The initial atomic layers of an epitaxially deposited film is usually coherent with the underlying matrix material, while the lattice of the film undergoes tetragonal distortion [25]. Further increases in the thickness of the deposited film stimulate the nucleation of dislocations, which partially relaxes the strain caused by lattice mismatch. Strained

epitaxial films are referred to as *pseudomorphic* when they are void of defects and the strain relaxes elastically, e.g. by tetragonal distortion [17].

Epitaxial material can accommodate a specific magnitude of elastic strain without the formation of defects such as dislocations. The critical thickness of an epitaxially grown thin film is the thickness at which the strained crystal begins to form misfit dislocations. The nucleation of misfit dislocations in epitaxial materials has been reported [17] to be generated above a critical thickness $d_c \propto \epsilon^{-1}$, where d_c represents the critical thickness of the strained layer and ϵ is the misfit strain. This implies that dislocations are induced due to the increasing strain in the material beyond the critical thickness. Misfit dislocations are line defects along which the crystal lattice is shifted [17]. Matthews and Blakeslee [26] proposed a model (also known as the M-B model) which examines misfit accommodation in epitaxial multilayers. Their model is widely used to describe the relaxation of a film with thickness beyond the critical thickness for lattice-mismatched epilayers.

In this model, the force exerted due to the misfit strain, F_{\in} , can be expressed as:

$$F_{\epsilon} = \frac{2G\left(1+\nu\right)}{1-\nu} \ bd\epsilon \cos\theta \,, \tag{3}$$

while the tension, F_l , in the dislocation line is approximately:

$$F_{l} = \frac{Gb^{2}}{4\pi (1 - v)} (1 - v \cos^{2} \alpha) \left(\ln \frac{d}{b} + 1 \right),$$
(4)

where

- *G* is the shear modulus of the epitaxial material,
- v is the Poisson ratio, expressed as $v = \frac{c_{12}}{c_{11}+c_{12}}$ (for isotropic cubic materials), and is $\sim \frac{1}{3}$ for most semiconductors. The parameters c_{11} and c_{12} are the elastic stiffness constants of the epitaxial material,
- *θ* is the angle between the slip direction and the direction in the film plane which is perpendicular to the line of intersection of the slip plane and the interface,
- *b* is the Burger's vector,

- *d* is the strained-layer thickness,
- ϵ is the misfit strain, and
- α is the angle between the dislocation line and its Burger's vector.

The maximum value of the strain is $\in_{max} = \frac{1}{2}\lambda$, where λ is the lattice mismatch. The critical thickness at which $F_{\in_{max}} = 2F_l$ can be derived from equation (3) and (4) as:

$$\frac{2G\left(1+\nu\right)}{\left(1-\nu\right)}bd\epsilon\,\cos\theta = 2\left(\frac{Gb^2}{4\pi\left(1-\nu\right)}\left(1-\nu\cos^2\alpha\right)\left(\ln\frac{d}{b}+1\right)\right)\tag{5}$$

Equation (5) can be simplified further to yield:

$$d\epsilon = \frac{b\left(1 - v\cos^2\alpha\right)}{4\pi\left(1 + v\right)\cos\theta} \left(\ln\frac{d}{b} + 1\right). \tag{6}$$

Substituting the expression $\in = \frac{1}{2} \lambda$ in equation (6) gives:

$$d_c = \frac{b\left(1 - v\cos^2\alpha\right)}{2\pi\lambda\left(1 + v\right)\cos\theta} \left(\ln\frac{d_c}{b} + 1\right) \,. \tag{7}$$

Equation (7) is the expression for the critical thickness at which $F_{\in_{max}} = 2F_l$. The critical thickness is determined by the degree of the mismatch, the dislocation properties in a material, and also by the elastic parameters of the material used.

2.6 Determination of the critical size of an Island

The processes and transition mechanisms undergone in the nucleation of 3D islands (such as QDs) has been the subject of significant interest. Numerous models have been formulated to explain the morphological transitions involving the formation of an island. They usually have complex and variable structures and are formed by strained layer growth processes. Optimal control of the size, shape and aspect ratio of these islands is fundamental in the fabrication of defect-free and coherent self-assembled QDs. However, precise control and a knowledge of the transition process is challenging due to the stochastic nature of the nucleation of these islands.

The critical size of an island or quantum dot is the size below which there is no morphological transition, but beyond which a morphological transition occurs. It is the
size where the island neither grows nor shrinks. The stages involved in the morphological transition of islands are mainly governed by the strain within the epilayer and substrate, which can be defined using thermodynamics and kinetics. The processes include the formation of the 2D wetting layer after deposition, and a gradual transition to 3D islands as a result of increased strain. The process is terminated by the ripening of islands, which are a few nanometres in size and are produced as a result of the self-assembly of semiconductor crystals. If there is a reduced misfit between the deposited material and the substrate, the average size of the islands and the critical size for morphological transitions will increase. Using the capillary model of 3D island formation, the critical size of an island can be expressed as [15]:

$$V^* = \left(\frac{\Gamma' \alpha'^{4/3} - \Gamma \alpha^{4/3}}{\alpha' - \alpha}\right)^3 \frac{1}{K^3 \in 6},$$
(8)

where

- *ϵ* is the misfit strain between the substrate and island materials,
- α' and α represent the facet inclination of two pyramidal islands relative to the surface of the substrate (where α < α'),
- Γ is a parameter containing the surface tensions of the island facets and wetting layer,
- Γ' represents the surface tensions of steep facets and is generally different from Γ, and
- *K* represents the elastic properties of the material.

Equation (8) reveals that the transition between shallow and steep morphologies transpires at a critical volume, which is proportional to ϵ^{-6} . The chemical potential of the island is given as:

$$\Delta \mu = \frac{\partial \Delta F}{\partial n} \,, \tag{9}$$

where ΔF is the total free energy of the island and *n* is the number of atoms contained in the island. Equation (9) assumes a negative sign when the nucleus is supercritical,

promoting an increase in the size of the island. However, a positive value of $\Delta \mu$ implies that the condition is not favourable for the addition of adatoms on the surface of the material. At the critical size *V**, the chemical potential, $\Delta \mu$, drops discontinuously, and the transition is of the first order. The decrease in chemical potential also implies that islands with steep morphology act as sinks for material, and their appearance leads to rapid coarsening of the ensemble and the consequent disappearance of smaller and shallower islands [15].

If the coherent growth of islands persists above a critical size, the growth will gradually degrade to incoherent growth, thus generating misfit dislocations. Supposing the influence of dislocation positions is taken into consideration based on the energy balance between the coherent and the dislocated states, the critical size for coherency can be obtained when the strain energy stored in the coherent quantum dot is equal to the energy in the dislocated one [27]. Also, if the size of the island is above a particular critical size, the electronic properties could be affected when the high misfit strain in the growing island is released via the nucleation of misfit dislocations. Similarly, above the critical size, the island edge is unstable [28]. This means that the island exhibits different values of energy variation as a result of alterations in its size or shape.

2.7 Structure and properties of InSb and GaSb

InSb is a direct, small band gap III-V semiconductor. The semiconducting properties of InSb were first reported in 1952 by Heinrich Welker [29]. It is known to be robust and exhibits a relatively high quantum absorption efficiency, with sensitivity in the MWIR region [4]. Similarly, GaSb, or gallium (III) antimonide, is classified as a direct, intermediate band gap semiconductor. Both InSb and GaSb crystallize in the zincblende structure shown in Figure 2.6.



Figure 2. 6. Zincblende structure of InSb and GaSb [30].

Chemical bonds in III-V compounds can be described to be mixed covalent-ionic in nature. InSb and GaSb are important III-V compounds that have been utilized for many purposes such as the fabrication of sensors and high speed electronic devices, due to their unique emission wavelength (within the IR region) and their high electron mobility. Tables 1 and 2 summarise some of the important physical properties of InSb and GaSb.

Parameter	Т (К)	InSb				
Crystal structure		Cubic (ZnS)				
Lattice constant (Å)	300	6.47877				
Coefficient of thermal expansion (10 ⁻⁶ K ⁻¹)	300	5.04				
	80	6.50				
Density γ (g/cm ³)	300	5.7751				
Melting point (K)		803				
	4.2	0.2357				
Energy gap (eV)	80	0.228				
	300	0.180				
Thermal coefficient of E_g	100 - 300	- 2.8 x 104				
	4.2	0.0145				
m_e^*/m_0	300	0.0116				
$m_{lh}*/m_0$	4.2	0.0149				
$m_{hh}*/m_0$	4.2	0.41				
Momentum matrix element P (cm ² /V.s)		9.4 x 10 ⁻⁸				
Electron mobility (cm ² /V.s)	300	8 x 10 ⁴				
	77	106				
Hole mobility (cm²/V.s)	300	800				
	77	104				
	77	2.6 x 10 ⁹				
Intrinsic carrier concentration (cm ⁻³)	200	9.1 x 10 ¹⁴				
	300	1.9 x 10 ¹⁶				
Refractive index		3.96				
Static dielectric constant		17.9				
Optical phonon (cm ⁻¹)						

Table 1: Physical properties of InSb [4].

LO (longitudinal)	193 (23.9 meV)
TO (transverse)	185 (22.9 meV)

Table 2: Physical properties of GaSb [4].

Parameter	T (K)	GaSb
Lattice constant (Å)	300	6.094
Density γ (g/cm ³)		5.61
Melting point (K)		985
Expansion coefficient		6.2 x 10 ⁻⁶
Thermal conductivity (WK ⁻¹ cm ⁻¹)		0.4
Energy gap (eV)	300	0.725
	0	0.822
Spin-orbit splitting energy, Δ_0 (eV)		0.76
Electron mobility (cm ² /V.s)	300	5,000
Hole mobility (cm²/V.s)	300	880
	77	2,400
Electron effective mass (m_e^*/m_0)	300	0.042
Hole effective mass		
Heavy hole mass (m_{hh}^*/m_0)		0.28
Light hole mass (m_{lh}^*/m_0)		0.05
Spin-orbit split mass		$0.13m_0$
LO phonon energy at zone center	300	28.8 meV
TO phonon energy at zone center	300	27.7 meV
		3.84 at 10 μm
Refractive index		3.79 at 2 μm
		3.92 at 1.55 μm
Dielectric constant		
Static dielectric constant	300	15.69
High frequency dielectric constant	300	14.44

2.8 Literature on InSb on a GaSb matrix

The growth of InSb on a GaSb surface follows the Stransky-Krastanov [24] growth scheme [31], which is a layer-by-layer growth mode followed by islanding. Most reported data for InSb dots in a GaSb matrix grown by both MBE [9] and MOVPE [32] mention a density of InSb/GaSb QDs in the 10⁹ cm⁻² range, with large lateral dot sizes (50-100 nm) [9]. Exceptions to this were reported by Shusterman [8] and Tasco [33], who reported QD densities of 10⁸ cm⁻² and 10¹⁰ cm⁻², respectively. The band alignment and emission wavelength of InSb/GaSb QDs have been the subject of some interest and controversy over the years. Some researchers showed that the band alignment of InSb/GaSb QDs is weakly type-I in nature [34], while another study reported these QDs to have a type-II band alignment [10]. The band alignment is important, since ultimately it determines the confinement energies, operating wavelength and overall performance of an optoelectronic device. Similarly, different photoluminescence (PL) peak energies have been reported. Some groups have reported emission in the near-infrared region (0.70 – 0.75 eV) [6] [7] [8], while other authors reported emission in the mid-infrared region (0.3 – 0.5 eV) [9]. Some of the previous reports [6] [7] [8] showing that InSb QDs emit in the near-infrared do not include direct evidence (such as TEM) of the formation of embedded QDs, while those that did include TEM images [35] [36] did not report detailed PL characterization, such as laser power and temperature dependent measurements. Child et al. [37], successfully confirmed the existence of excited states in the InSb/GaSb QD system by measuring the intra-dot transitions. Also, the MOVPE growth of InSb QDs using GaAs substrates with a 1.5 µm thick GaSb buffer layer was reported by Alphandery et al. [6], who established that the optimum QD PL intensity at an energy of 0.738 eV was obtained for a \sim 3 second deposition, with the growth rate of InSb estimated to be between 1 and 2 monolayer per second (ML/s). These authors used magneto-PL to determine the QD size and to prove that the luminescence originated from the QDs. Shusterman *et al.* [8] reported the growth of a high-density of InSb-based nanostructures by MOVPE, using the droplet hetero-epitaxial (DHE) mode. The best results in terms of size control and dot density of InSb dots grown on InAs, GaAs, GaSb, InAsSb and InSb substrates were obtained on As-based substrates. It was also found that reductions in the III/V ratio and growth rate for self-assembled InSb QDs grown on a GaSb matrix by MOVPE, resulted in a change of the morphology of the InSb islands from hillocks without facets, to dumbbell shaped islands with distinct facets [32].

Table 3: Summarized table of reported data on InSb dots in a GaSb matrix, containing important experimental results such as the PLenergy, density of dots, growth method and other relevant information.

Year	Growth	Growth	InSb QDs		Density	Density Characterised	PL energy		ed PL energy		Temp	Growth time(s)	Ref
	rate (ML/s)	method	Width (nm)	Height (nm)	(cm ⁻²)		QD (eV)	WL (eV)	(°C)				
1998	-	MBE	~80	~12	-	AFM ¹ , TEM ²	0.75	0.79	420	-	[35]		
1999	1 – 2	MOVPE	20-30	2 - 4	-	AFM, TEM	0.738	-	480	1 - 5	[6]		
2001	1 – 2	MOVPE	47	28	5×10 ⁹	AFM, CTEM ³ , HRTEM ⁴	-	-	490±10	-	[32]		
2003	-	MOVPE	38	4	1×10 ⁹	AFM	0.73	0.757	-	-	[37]		
2004	1 – 2	MOVPE	20-30	2 - 4	5×10 ⁹	AFM, TEM	0.74	0.77	480	3 - 4	[7]		
2006	0.33	MBE	40-80	10-15	4×10 ⁹	AFM, TEM	0.75	-	450	~20 - 50	[9]		
2006	-	MOVPE/droplet epitaxy	25-50	10-15	7×10 ⁸	AFM, HRSEM,HRTEM	~0.73	0.75	460-480	-	[8]		
2007	~0.3-1.2	MBE	~50	8	~1-3×10 ⁹	AFM, TEM	0.367, ~0.5	0.72	~370 - 450	~20 - 50	[10]		

¹ Atomic force microscopy

² Transmission electron microscopy

³ Conventional transmission electron microscopy

⁴ High resolution transmission electron microscopy

A finite element method has been used to simulate the strain field in InSb/GaSb QDs [38]. The dots were simulated in the framework of anisotropic elasticity, before and after the onset of plastic relaxation. The model was used to determine the equilibrium critical size of the dots and to directly calculate the residual strain in the dislocated system. A plot of total energy versus the QD base diameter, obtained before and after the onset of plastic relaxation using the above mentioned approach gave a value of 11.4 nm (in agreement with experimental data) as the critical base diameter of InSb/GaSb QDs. Intermixing of In-Ga was assumed to occur near the interface. In another report, the deposition of ~2 monolayers (ML) of InSb on the GaSb (100) surface using MBE was observed to produce a 2D-3D growth mode transition, leading to the formation of 3D InSb islands which were ~80 nm in diameter [35]. A further increase in the thickness of the InSb layer to more than 3 ML was reported to cause a dramatic drop in the PL intensity, resulting from plastic relaxation of the islands.

The incorporation of a thin InAs QW, strongly coupled to an InSb/GaSb QD system, has been reported to facilitate a reduction of the low temperature PL emission energy from 0.72 to 0.48 eV [39]. Furthermore, low excitation power PL measurements from selfassembled InSb QDs grown on a GaSb matrix by MOVPE have illustrated that the PL is dominated by the lowest QD transition energy, and that the emission energy increases in energy by ~ 11 meV with an increase in the excitation power [40], a behavior attributed to the large size distribution of QDs and the progressive population of states in smaller dots as the temperature and laser power increases. The first far IR modulated (FIRM) PL measurements in InSb/GaSb QDs were performed by Child et al. [41], and it was found that at low power densities, the FIR absorption stimulates the movement of carriers between dots and effectively cools the system electronically, resulting in the preferred population of larger, low energy dots and thus increasing the PL intensity. By monitoring the transmission spot intensity in reflection high energy electron diffraction (RHEED) experiments as a function of substrate temperature, high temperatures (> 475 °C) were used to deduce the desorption point of In from InSb in relation to an internal temperature reference. This was done during the investigation of the 2D–3D growth mode transition occurring during the growth of InSb on a GaSb matrix using MBE, where a critical thickness of 1.7 ML for the 2D-3D transition was determined for optimum growth conditions [31].

An increase in the thickness of the InSb QDs grown on a GaSb matrix using MBE was found to cause the QD PL line to shift to longer wavelengths (from 0.75 eV to ~0.73 eV). This was accompanied by broadening of the line widths from ~25 meV to ~40 meV [42]. The PL behavior was attributed to an increase in the dimensions of the newly formed QDs and an increase in the size dispersion. Calculations done for fully strained InSb/GaSb QDs have shown that the system has weakly type-I band alignment [34]. The calculations were carried out for three different geometries (QWs, QWRs and QDs) and the confinement energies were estimated by computing the mean effective masses. This result is in contrast with reports from Deguffroy *et al.* [10], where a type-II alignment with a low (mid-IR) transition energy was used to describe both the PL and electroluminescence (EL) emission spectra from InSb/GaSb QDs grown using MBE.

Finally, Tasco *et al.* [9] [33] developed a multi-step MBE growth technique which permits the growth of InSb/GaSb QDs with high structural perfection and high density. They also measured PL and EL emission from InSb/GaSb dots at 360 meV with a corresponding linewidth of 47 meV at 90K. The emission was detected up to room temperature. A summary of the results obtained from most of the research completed for InSb/GaSb QDs has been presented in Table 3. This table clearly reveals that there is still much to be done to fully understand the physical properties, particularly the optical properties, of InSb/GaSb QDs.

Chapter 3

Metal-organic vapour phase epitaxy

3.1 Introduction and background

Chemical vapour deposition (CVD) is a technique that produces a solid material (in the form of either a thin film, powder, or single crystal) on a substrate material via a chemical reaction, using vapour phase precursors. Metal-organic chemical vapour deposition (MOCVD) is a special type of CVD which involves the use of metal-organic precursors. MOVPE, also known as organometallic vapour phase epitaxy (OMVPE), is an MOCVD process that involves the formation of single crystal epitaxial films on a crystalline substrate by using metal-organic precursors [43]. The MOCVD technique was first introduced in 1968 for the growth of compound semiconductor materials and devices from the vapour phase [44]. This technique was originally named MOCVD by Manasevit to highlight the metal content of the sources and to ward off complications with organometallic chemistry research, which was known to place more emphasis on higher order organic radicals [45]. MOCVD came into the limelight in the late 1980s as a competitive technique for the growth of high quality semiconductor materials. Much of this success can be attributed to the painstaking work which has been carried out over many decades to improve the purity of organometallic precursors and hydrides [46].

MOVPE/MOCVD plays a vital role in the manufacturing process for III-V compound semiconductors and is an effective method used for the fabrication of QWs and superlattices, QWRs and QDs with a high degree of uniformity and structural integrity [47]. The technique is used in the fabrication of solar cells, light-emitting diodes (LEDs) and transistors [45]. Its working mechanism involves the extraction of chemical elements from metal-organic precursors and hydrides, which are vaporised and transported into the reactor via a carrier gas (usually ultrapure) at elevated temperatures.

Most often, the mode of gas streaming in a horizontal MOVPE reactor chamber takes the form of laminar flow across the heated susceptor, which is a desirable attribute for efficient pyrolysis of the precursors. Similarly, the properties of the deposited crystal, which are approximately close to atomic scale, can be altered by modifying the concentrations and types of source vapours introduced into the reactor. For a vertical reactor chamber, the introduced gases enter from the top and are deflected by a baffle prior to moving downwards towards the heated susceptor. The gas flow is constrained to the sides by the susceptor, while the velocity profile in the system is dependent on the geometry of the reactor [45]. The MOVPE growth technique is suitable for the development of superlattices, quantum wells, wires and dots, with the required changes in material composition controllable on the atomic scale. MOVPE offers the flexibility for device fabrication through alterations of the band structure. According to Stringfellow [48], MOVPE is also suitable for producing high-quality nitrides for the highest performance short-wavelength photonic devices. It is also more suited for large-scale production than other epitaxial techniques [48].

3.2 Design and working mechanism of the MOVPE growth system

The configuration of the Thomas Swan MOVPE system used in this research, which can be operated manually or optionally by computer control, is depicted in Figure 3.1.



Figure 3. 1. Simplified schematic diagram of MOVPE system configuration.

Nitrogen is used as the inert sweep gas, while palladium-diffused hydrogen is used as the carrier gas. The flow rate of the palladium-diffused hydrogen is controlled to conform to a desired set flow rate by a mass-flow controller, which feeds three-way valves on each of the metalorganic source bubblers. The ultra-pure hydrogen is channelled through bubblers immersed in a temperature controlled bath via the inlet line of the three-way valve, and the precursors are transported through the outlet line to a solenoid valve, which feeds the manifold where the gases mix before reaching the reactor. The trimethylindium (TMIn) line is connected to an EPISON III gas-flow monitor, in order to regulate the pick-up rate of the source. This helps to compensate for the fluctuation of the TMIn concentration in the bubbler, which has been reported to change with time [49]. The rectangular quartz reactor houses a molybdenum susceptor, drilled to accommodate a thermocouple which is confined within a quartz sheath. The quartz acts to isolate the thermocouple from the gaseous environment inside the reactor.

The mixed gases conveying the precursors are introduced from the manifold into the reactor at elevated temperatures, which enables the molecules to pyrolyze, thus depositing the desired atoms on the surface of the substrate, which is placed on the susceptor. This process is accompanied by the removal of any precursor that was not cracked from the reactor to either the vent or the reactor pyrolysis furnace, for further decomposition. The decomposed materials from the furnace are filtered and finally discarded through the exhaust into the atmosphere.

3.3 Brief comparison between MBE and MOVPE

The MBE growth technique involves the epitaxial deposition of compound semiconductor materials or device structures within an ultra-high vacuum system where the layers are monitored using reflection high energy electron diffraction (RHEED). In MBE, streams of molecules or atoms emanating from the evaporation sources impinge simultaneously onto a heated crystalline substrate [22]. The composition and thickness of the film is determined by regulating the individual fluxes [50]. The first reported self-assembled QDs were grown using an MBE growth system [51].

Table 4 summarises the significant differences between the MBE and MOVPE growth techniques. The two growth techniques are known to produce similar results in the hands

of experts, while their respective limitations are usually attributed to those significant to the materials used, rather than the technique itself [45].

MBE	MOVPE			
Does not involve the use of carrier gases.	Involves the use of carrier gases.			
The thickness of each layer can be	Film thickness cannot be directly			
directly controlled with precision.	controlled with precision.			
The growth of the crystals is by physical	The growth of the crystals is by chemical			
deposition.	reactions.			
Growth process occurs in an ultra-high	Growth process occurs in a gaseous			
vacuum, allowing in-situ monitoring of	environment.			
the evolution of the developing film.				

Table 4: Table of comparison between MBE and the MOVPE growth techniques.

3.4 A review of the advantages and challenges of MOVPE

MOVPE is the epitaxial crystal growth technology of choice for the production of many commercial devices [45]. Most compound semiconductor materials have been fabricated successfully by MOVPE. It has a number of key benefits that makes it a suitable technique in research, development and production [52]. The technique is effective in assembling multi-layer and graded composition layers [53] of semiconductor compounds that is well suited for the design of a material with specific optical and electrical properties. It also offers more flexibility in terms of deposition conditions when compared to other techniques. These properties make it easier to systematically study the growth process of the crystalline layer deposited. Similarly, it offers selective *in situ* monitoring and is known to be viable for the large-scale production of materials. The growth process has been established to be thermodynamically promising due to the higher growth temperatures typically employed. This attribute increases the growth rate and is economically advantageous compared to MBE. Similarly, MOVPE has the ability to handle materials with high vapour pressures, such as lead (Pb) [54], can be used to produce conformable coatings [55], and is an established technology beneficial for large-area deposition [56].

Despite the advantages and successes achieved by MOVPE there are still challenges, which include the dependence of the quality of materials produced on the availability of well-suited, high-purity precursors. Similarly, most of the gases used are highly corrosive and toxic, which makes them hazardous to handle. The process is complex and susceptible to carbon and hydrogen contamination. The technique also involves the control of many parameters. Moreover, the absence of RHEED in most MOVPE systems makes it difficult to monitor and control the growth rate. Finally, compared to MBE, the interfaces between different compounds are not as abrupt because of their dependence on gas flow.

3.5 MOVPE growth parameters

Crystal growth using MOVPE is complex and therefore not all aspects of the process are thoroughly understood [48]. However, as a result of intensive research, various useful models have been formulated to enable a more accurate prediction, knowledge and control of the growth process. Many parameters play important roles in determining the dynamics and rates of the chemical reactions during MOVPE growth. Some of these will be summarised briefly in this section.

3.5.1 Growth temperature

This is the actual temperature on the surface of the substrate measured during the growth process. The effective growth temperature of the layer growing on the substrate is the key parameter which governs the growth rate. An appropriate temperature range is essential to trigger a systematic pyrolysis reaction, which causes efficient decomposition of the precursor materials. The presence of a heated substrate/epilayer surface results in a sink for reactive constituents, which leads to concentration gradients that define the growth rate of the material deposited [45]. This implies that growth temperatures above that which is required activates uncontrolled reaction rates, while very low growth temperatures result in low surface mobilities. Furthermore, it has been reported that TMSb decomposes effectively at temperatures above 400°C in H₂ ambient [57], while a temperature of 460°C is required for the decomposition of trimethylgallium (TMGa) in H₂ ambient [58].



Figure 3. 2. Growth rate of GaSb as a function of growth temperature [59].

According to experimental results obtained by Cooper *et al.* [59], the growth rate of GaSb is directly dependent on growth temperature (Tg), as shown in Figure 3.2. It was also observed that the growth rate increased with a decreasing V/III ratio. Chiang and Bedair [60] used TEIn and TMSb sources in a vertical atmospheric pressure MOVPE reactor and showed that the growth rate of InSb was dependent on the TMSb flow at a constant TEIn concentration, while Biefeld [61] demonstrated that the growth rate was directly proportional to the flow rate of TMIn. Likewise, growth rates have been reported [62] to be dependent on factors such as the concentration of the group III alkyl precursor (TMGa), reactor pressure, growth rate of GaSb (with TMGa and TMSb as metalorganic sources) using a horizontal MOVPE system at atmospheric pressure has been reported [63]:

$$R_{g} = k_{GaSb} \frac{K_{Ga} K_{Sb_{4}} P_{TMGa} P_{TMSb}}{(1 + K_{Ga} P_{TMGa}) (1 + K_{Sb_{4}} P_{TMSb})}$$
(10)

where

- *k_{GaSb}* represents the rate constant for the surface reaction,
- K_{Ga} and K_{Sb_4} are the adsorption equilibrium constants of Ga and Sb₄,
- *P*_{*TMGa*} and *P*_{*TMSb*} are the partial pressure of TMGa and TMSb.

Equation (10) was derived with the assumption that the pyrolytic reaction of both TMGa and TMSb (which decompose to form Ga and Sb₄, respectively) are homogeneous in the gas phase. Equation (10) shows that the growth rate is proportional to the surface coverage of Ga and Sb₄ species [63]. This implies that an increase in TMSb mole fraction would give rise to an increase in Sb₄ surface coverage ($K_{Sb_4}P_{TMSb} \gg 1$).

3.5.3 V/III ratio

In simple words, the V/III ratio can be described as the input molar ratio of the group V and group III precursors. The stoichiometry of compound semiconductors is fundamental in the MOVPE growth process and its optimisation is necessary in order to obtain high quality layers that are free from defects. The fabrication of Sb-based compounds using MOVPE is challenging due to the very low surface mobility and non-volatility of elemental antimony as compared to As or P in the GaAs- and InP-containing material systems [64]. This implies that only a very narrow range of V/III ratios and growth temperatures can be used for obtaining layers with high surface morphology.

A very narrow range of V/III ratios in the vapour phase (2 to 3) was reported for obtaining high mobility epitaxial layers of InSb on GaAs substrates by MOVPE, using TMIn and either triethylantimony (TESb) or trimethylantimony (TMSb) as source precursors [65], and at growth temperatures of 400°C and 470°C for TESb and TMSb, respectively. The samples were separately prepared in two different MOVPE systems, namely a horizontal, atmospheric pressure system with a quartz reactor tube, and a vertical 4.5 inch diameter stainless steel chamber. The choice of growth temperature used in each case was ascribed to the lower thermal stability and vapour pressure of TESb compared to TMSb; the latter is known to have a larger vapour pressure and growth rate. Hall mobilities of up to 60 900 and 27 000 cm²/V s were measured at 300 and 77 K,

respectively. The best surface morphology was obtained at a V/III ratio of 3. A TEIn/TMSb ratio of 1.28 was reported to produce optimal morphologies at 460°C for the homo-epitaxial growth of InSb in a vertical atmospheric pressure MOVPE reactor [60]. The relevance of high-purity precursors and careful optimisation of the V/III ratio across the susceptor was emphasised in a study on high mobility InSb by Gaskill *et al.* [66], where an optimum V/III ratio of 7.4 was required for InSb layers grown at 450°C on InSb substrate.

3.5.4 Reactor pressure

The reactor pressure is the pressure inside the growth chamber during the growth process. To achieve the growth of a high quality layer, one of the essential parameters that needs to be controlled during MOVPE is the reactor pressure. The reactor pressure influences the growth process and the reactions on the surface of the substrate. Other factors affected by the reactor pressure includes the temperature in the vapour stream and the flow pattern and flow rate of the carrier gas.

To prevent parasitic reactions which are prevalent at atmospheric pressure, especially when using triethyl-group III precursors, a low reactor pressure is often vital to either minimise or completely prevent these premature reactions [48]. This is a result of a reduction in the number of gas-phase collisions before the precursor species reach the substrate. This improves the uniformity and lateral homogeneity of the deposited layers, which means that a low reactor pressure is crucial for large-scale reactors. However, the rate of pyrolysis of the group V hydrides is remarkably decreased for low reactor pressures, and thus demands the use of exceptionally high values of V/III ratios, often above 100 (typical for the growth of gallium arsenide(GaAs) using TMGa), in the input gas stream [48]. Likewise, low values of the V/III ratio (< 1.0) are required during low pressure growth of GaSb (using TMGa and TMSb) to prevent complications arising from the reduced sticking coefficients of Ga and Sb atoms on the growth surface (with Ga more affected than Sb) [62].

3.5.5 Substrate orientation

Substrate orientation is the surface plane index and tilt angle of the substrate towards a certain direction, usually with an error range indicated (e.g. (100) 2° off towards <111>

 \pm 0.1°]. The orientation of the substrate can determine the efficiency of the growth kinetics and surface reactions during the growth process. The surface morphology and growth rate of the deposited layers will therefore depend on substrate orientation.

Substrate mis-orientation has been reported to cause a reduction in surface diffusion, which resulted in a bimodal size distribution of InAs QDs on GaAs substrate [(100) 2° tilted towards <110>] [67]. Similarly, migration of adatoms on the surface of mis-oriented substrates has been reported to be restricted because of the energy barrier which exists at step kinks [68]. All substrates used in this work were supplied by "Galaxy Compound Semiconductors" in the USA, with orientations of (100) \pm 0.1°, (111) \pm 0.1°, and (100) 2° off towards <111>B \pm 0.1°, respectively. The effect of GaSb substrate orientation on the growth of InSb QDs will be discussed in more detail in Chapter 6 of this work.

Chapter 4

Experimental methods and characterisation techniques

In this chapter, the description of the experimental procedures used to prepare the samples and the characterisation techniques used to study their properties, are presented. The design and operating principles of the MOVPE system used, were summarised in Chapter 3.

4.1 Choice of precursors, V/III ratios and growth rates

Efficient pyrolysis of the precursors and a low level of carbon contamination are desirable for the MOVPE growth of III-V semiconductors. In this study, trimethylindium (TMIn), triethylgallium (TEGa), trimethylantimony (TMSb) and trisdimethylaminoantimony (TDMASb) were used as source precursors.



Figure 4. 1. Vapour pressure versus temperature plots of group III and V precursors [48].

Figure 4.1 are plots which show the temperature dependence of the vapour pressure for some of the commonly used III-V organometallic sources. According to Figure 4.1, the trimethyl sources (especially for group III organometallics) have higher vapour pressures than the triethyl sources. The choice of trimethyl sources (TMIn and TMSb) in this study stems from the fact that they are less likely to be involved in parasitic reactions. Their excellent stability allows them to be stored at room temperature over an extensive period of time prior to use [48]. TDMASb is an ideal precursor for low temperature growth of antimonides using MOVPE. However, it has a low vapour pressure of only 0.75 Torr at 20°C [48], while TEGa and TMSb are the preferred source combination for the growth of GaSb due to the mass-transport limited growth in a reasonable wide range from 525°C to 640°C [69].

For values of V/III ratio between 0.77 and 2.4, the growth rate of InSb prepared in a vertical quartz reactor at atmospheric pressure using MOVPE has been reported [61] to be a linear function of TMIn flow rate. To obtain optimum growth conditions, the choice of V/III ratio is very important, and it depends on the growth conditions, organometallic sources and the reactor design. Therefore, to establish an appropriate V/III ratio for various growth parameters, several series of thick calibration layers were grown and analysed in this study. Further details on the V/III ratio used and the respective growth rates will be presented and discussed in Chapter 5. The precursors (TMIn, TEGa, TMSb and TDMASb) used in this study were immersed in a temperature controlled bath containing propylene glycol at temperatures of 25, 9.8, -11.5, and 23°C respectively. The TMIn and TDMASb gas lines are heated to slightly higher temperatures (above 33°C) compared to the temperature of their bubblers. This prevents condensation of the organometallics along the lines.

4.2 Substrate preparation

Three different types of GaSb substrates were used in this study: GaSb [(100) \pm 0.1°, (111) \pm 0.1°, and (100) 2° off towards <111>B \pm 0.1°]. Prior to growth, the substrates were degreased by sequential immersion in trichloroethylene, acetone and methanol, and then rinsed with deionised water. This was followed by etching the substrate with HCl (37% concentration) for 5 s to remove the native oxide layer and defects which might have been induced as a result of chemo-mechanical polishing. After etching, the substrates were

rinsed in deionised water, blown dry with N_2 and immediately placed on a molybdenum susceptor and loaded into the quartz reactor.

4.3 Growth procedure

Once the substrates were in the reactor, the reactor was purged with H₂ for 300 s and the substrates were then annealed for 600 s at 550°C to remove lingering oxides and water vapour from the system. The overall growth procedure was controlled by computer. This was done in order to enable consistent and precise control of the timing of each step, due to the high sensitivity of the structural and optical properties of the samples to the epitaxial growth sequence. The precursors were transported to the horizontal quartz reactor using palladium-diffused H₂ as the carrier gas, with a total H₂ flow rate of 2.15 standard litres per minute (SLM). In order to prepare the lines, a stable flow within the bubblers and the lines was first established. The growth run was launched by first transporting the precursors from the bubblers through the vent line for \sim 240 s, before channelling it into the quartz reactor. The substrate temperature during the growth process was varied, depending on the melting point and cracking temperatures of the precursors used. Temperature control was achieved using a proportional-integralderivative (PID) temperature controller and a type-K thermocouple embedded in the molybdenum susceptor. The precursors were channelled out of the reactor after the growth process, and the temperature of the reactor was reduced to room temperature, while the samples were cooled by purging the system using H₂. The purging also served to eliminate residual metalorganics from the reactor. During the period of this study, \sim 400 growth runs were performed.

4.4 Characterisation

4.4.1 Photoluminescence (PL) spectroscopy

PL spectroscopy is one of the basic characterisation techniques used to study the discrete energy levels in QDs. It is a non-destructive method, which permits an intensive investigation of the material's electronic structure using laser light to excite electrons in the material from the valence band into the conduction band. The electrons, on absorption of energy from the incident light, are raised to excited states and subsequently return to the ground state by emission of radiation. The process of emission is through the release of energy in the form of photons.



Figure 4. 2. Schematic diagram of PL set-up used in this study.

Figure 4.2 is a schematic diagram representing the PL set-up used in this work, with the most important components shown. The system is controlled using a computer that communicates with and controls the monochromator with the help of a General Purpose Interface Bus (GPIB) connector. Samples are mounted in a closed-cycle helium cryostat furnished with fused optical quartz windows, and a 532 nm diode pumped solid state laser (EXLSR-532-200-CDRH) is used as an excitation source. The laser beam intensity is modulated using an SR540 optical chopper controller equipped to maintain a precise chopping frequency which also serves as a reference signal, using a motor speed control design. The modulated laser beam is then focused onto the sample using an adjustable mirror and an iris diaphragm (with adjustable aperture). The intensity of the beam is attenuated using neutral density filters, while the PL emission from the sample is collimated and focused onto the entrance slit of a fully automated Czerny-Turner type

monochromator (Horiba FHR1000) with a focal length of 1 m. A high pass filter in front of the entrance slit of the monochromator removes unwanted reflections from the laser beam. A liquid nitrogen cooled germanium photodetector is used to detect the PL signal, and a lock-in amplifier (SR530) improves the signal-to-noise ratio of the detected signal. The final output, which is measured in the form of intensity (amplified detector signal) versus photon energy or wavelength, is displayed on a computer screen.



4.4.2 Scanning probe microscopy (SPM)

Figure 4. 3. Working mechanism of SPM.

Figure 4.3 illustrates the working principles of an SPM system. In this work, a Bruker Dimension Icon SPM system was used to study the surface features of the uncapped dots, their size distribution and dot density. SPM is a generic name given to microscopy techniques which can be used to image topography or other physical features of nanoscale structures and surfaces with almost atomic resolution, by using a physical probe, usually in the form of a nanoscale tip. The tip which serves as the probe is mounted on the end of a cantilever, as shown in Figure 4.3.

The movement of the tip back and forth on the sample is precise and accurate to an atomic scale and is controlled by voltages applied to the X and Y electrodes on the piezoelectric tube, which deflects the tube horizontally. The voltage applied to the Z electrodes on the

piezo tube is used to control the vertical height of the tip. The deflection distance of the cantilever is measured through the reflection of a laser from the top of the cantilever. The reflected laser beam is detected by an array of photodiodes, generating a sinusoidal electronic signal. The deflections of the cantilever can be caused by mechanical contact, chemical bonding, or by forces such as electrostatic, magnetic and Van der Waals forces. The most common SPM techniques are:

- Atomic Force Microscopy (AFM), which measures the interaction forces or electrostatic forces between the cantilever tip and the surface of the sample.
- Scanning Tunnelling Microscopy (STM), which measures a weak electrical current flowing between the tip of the cantilever and the sample.
- > Magnetic Force Microscopy (MFM), which measures magnetic forces.
- Near-Field Scanning Optical Microscopy (NSOM), which is used to scan and measure a very small light source close to the sample.

The two primary modes in SPM are the contact mode and the tapping mode. All samples used in this work were analysed using the tapping mode.

4.4.3 Transmission electron microscopy (TEM)

TEM involves the utilisation of electron beams to resolve structures by transmitting the electrons through an electron transparent sample. It consists of a thermally assisted field emission electron source, electromagnetic round lenses to shape the electron probe and image it onto the specimen surface (in scanning mode) and a projection system to image the diffraction pattern onto a high angle annular dark field (HAADF) or bright field (BF) detector, which collects the diffracted and undiffracted beams, respectively. During sample preparation, the original bulk samples were thinned down to about 100 nm or less in order to be sufficiently electron transparent. A double Cs corrected JEOL ARM 200F TEM and a Philips Tecnai 20F FEG TEM were used in this study to investigate features such as the crystal structure of the grown layers, their composition and the presence of defects such as dislocations in capped samples. The TEM micrographs were taken under both high angle annular dark-field (DF) and bright-field (BF) imaging conditions in scanning mode, while the compositional information was extracted using direct analytical measurements by means of energy-dispersive X-ray spectroscopy (EDS). The instrument was operated at 200 kV in scanning mode and an Oxford instruments X-

Max 100 TLE SDD was used to obtain energy dispersive X-ray spectra. This data was processed using Aztec software from Oxford instruments. Lamellae for electron transparency were prepared using a focused ion beam (FIB), protecting the sample surface through pre-deposition of a platinum (Pt) layer, and milling with Ga+ ions close to normal incidence.

4.4.4 Band edge simulations

By applying the self-consistent Schrödinger and Poisson equations, the band alignment, energy levels, and carrier wave functions of the samples in this work were modelled theoretically using the nextnanomat software (version 3.1.0.0). Nextnanomat is a graphical user interface (GUI) software programmed in C#, used for editing input files, quick visualisation and organisation of simulation results. It was developed and written at the Walter Schottky Institute of the Tehnische Universität Munchen, Germany and is customised to work with other software packages such as nextnano³ (written in Fortran), nextnano++ (written in C++), nextnano.MSB and nextnano.QCL. The software is capable of providing information on the energy levels in pyramidal and cuboidal shaped QDs, strain and piezoelectric fields, optical inter-band transitions in a QW, and the quantum confined Stark effect, amongst others. Visualisation features can be displayed in either 1D, 2D or 3D data output. Apart from finding applications in optoelectronics and quantum cascade lasers (QCL), other applications of nextnanomat software include analysis of solar cells, quantum computing and bio chips.

4.4.5 Scanning electron microscopy (SEM)

Another type of imaging technique used to study surface topography and composition of samples is SEM. It consists of an electron gun through which an electron beam is accelerated down the column towards a series of lenses (condenser and objective) which act to control the diameter of the beam as well as to focus the beam on the sample. The data acquisition and imaging utilise an electron beam that scans the surface of the sample in a raster pattern, and thus, the 3D images are produced based on scattered electrons detected by a detector, unlike in TEM where the electron beam passes through the sample. For characterisation, a JEOL JSM 7001F FEGSEM was used in this study. A typical

secondary imaging accelerating voltage of \sim 5.0KV, a working distance (WD) of 6 or 10 mm, and a current of \sim 100 pA was used for each scan.

4.4.6 X-ray diffraction (XRD)

The crystalline quality of all epitaxial calibration layers (with thickness of \sim 2.5 µm and above) were evaluated using a Bruker D8 Discover X-ray diffractometer. XRD is a nondestructive structural analysis technique which furnishes information on statistical averages of large ensembles via the interaction between the incident beam of X-rays and the atomic planes of the crystal. X-rays which are used in XRD instruments are produced as a result of the excitation of inner core electrons in the target atoms. The vacancies produced (in the n = 1 or K-shell of the atom) as a result of the ejection of electrons during bombardment, are abruptly filled through the transition of electrons from higher levels (e.g. n = 2 to n = 1) to fill the empty states. During these transitions, X-rays (often referred to as "characteristic X-rays") having frequencies which correspond to the difference in atomic energy levels of the target atoms. X-rays can also be produced by the sudden deceleration of electrons when they interact with the target atoms; this is called "bremsstrahlung" or "braking radiation". The latter is not applicable to XRD instruments. Information such as the crystallinity, composition, interatomic spacing, residual stress, crystallite size and average orientation of the crystallites can be deduced using this technique. The Bruker D8 Discover high resolution XRD system makes use of two different detectors namely the Pathfinder and LynxEye detector. In this work, the XRD diffractometer was operated at 40 kV and 40mA, while the LynxEye detector was used for obtaining the X-ray diffraction patterns and the Bragg peaks/angles from the epitaxial layers.

Chapter 5

Determination of optimum growth conditions for InSb quantum dots

5.1 Chemistry of precursors

The choice and knowledge of the precursors used during any MOVPE growth process are vital and play a significant role in determining the quality of the deposited epitaxial material. Certain criteria are fundamental when determining the choice of precursor to be used. Some of the properties of an ideal precursor are a low degree of toxicity, good thermal stability, non-pyrophoric, good volatility, high purity, preferably recyclable and stability in its container to prevent the need for a special storage facility. Also, the choice of growth temperature is often governed by the pyrolysis temperature of the precursors employed, while the pyrolysis temperature is linked to the nature of the metal-carbon bond strength in the precursor molecule [48]. The summary of precursor chemistry presented here will be limited to TMIn, TEGa, TDMASb and TMSb, which are the precursors used in this work. Table 5 presents a summary of the fundamental properties of these precursors.

Table 5: Vapour pressure and other physical properties of the precursors used in thisstudy [43] [70].

Precursor	Formula	Physical	Main	Density	Vapour		Bond
Acronym		State at	Hazard	(gcm ⁻³)	Pressure		Strength
		300 K			Log10P(1	nmHg)	(kcal/mol)
					= A - B/7	ſ (K)	
					A	В	
TMIn	(CH3)3In	Solid	Pyrophoric	1.568	10.52	3014	47
TEGa	(C2H5)3Ga	Liquid	Pyrophoric	1.06	8.08	2162	57
TDMASb	[(CH ₃) ₂ N] ₃ Sb	Liquid	Flammable	1.3	6.23	1734	-
TMSb	(CH ₃) ₃ Sb	Liquid	Pyrophoric	1.528	7.7068	1697	57

5.1.1 TMIn

TMIn ((CH₃)₃In) is a group III precursor that is a solid at room temperature. It melts at 88.4°C and has a boiling point of 133.8°C [70]. Unlike triethylindium (TEIn), which is a liquid at room temperature and has an extremely low vapour pressure, TMIn has a relatively high vapour pressure and is known to be void of parasitic reactions. This attribute has resulted in its wide use as a precursor source for indium.



Figure 5. 1. Percentage decomposition of TMIn as a function of temperature in H₂ and N₂ ambients [71].

A study by Larsen *et al.* [71] showed that the homolytic decomposition of TMIn occurs at a lower temperature in a H₂ ambient than in a N₂ ambient. This is illustrated in Figure 5.1, where 100% of TMIn is completely decomposed at 380°C. This was attributed to the weak bond strength of In–CH₃. The decomposition of TMIn in a H₂ ambient was described via a chain reaction process by Buchan *et al.* [72]:

$$In(CH_3)_3 \to CH_3^* + In(CH_3)_2^* \tag{11}$$

$$CH_3^* + H_2 \rightarrow CH_4 + H^* \tag{12}$$

$$H^* + In(CH_3)_m \to CH_4 + In(CH_3)_{m-1} \quad m = 1, 2 \text{ or } 3$$
 (13)

From equations (11), (12) and (13) it was proposed that the invasion of TMIn by H radicals (H*) played a role in the reduction of the TMIn pyrolysis temperature in a H_2 ambient [72].

5.1.2 TEGa

TEGa ((C₂H₅)₃Ga) is a group III precursor that is a liquid at room temperature. It has melting and boiling points of -82.3° and 143°C, respectively [70]. The decomposition of TEGa was studied using a quadrupole mass analyser and was reported to occur between 220°C and 330°C in a H₂ ambient [73]. According to a study by Lee *et al.* [74], the mechanism of decomposition for TEGa can be described by two different reaction paths, firstly by a loss of ethyl radicals:

$$Ga(C_2H_5)_3 \to Ga(C_2H_5)_2 + C_2H_5^*$$
 (14)

The ethyl radicals produced in equation (14) can further recombine with H₂ as follows:

$$C_2 H_5^* + H_2 \to C_2 H_6 + H^*$$
 (15)

The second reaction path can occur via β -elimination [75], which involves the creation of ethene by replacing the Ga-C bond in equation (14) with a Ga-H bond, i.e:

$$Ga(C_2H_5)_3 \to GaH(C_2H_5)_2 + C_2H_4$$
 (16)

5.1.3 TMSb

TMSb ((CH₃)₃Sb) is a group V precursor with a relatively high vapour pressure. The melting and boiling points of TMSb have been reported to be – 86.7° and 80.6°C, respectively [70]. A study of its decomposition using a mass spectrometer revealed that pyrolysis occurs at temperatures above 400°C, depending on the carrier gas, as shown in Figure 5.2 [57]. This figure shows that 50% of TMSb is decomposed at 450°C in a H₂ ambient. A report by Graham *et al.* [76] illustrated that the growth of InSb using TMSb is unsuitable at growth temperatures below 450°C. The presence of TMSb was also reported [57] to retard the pyrolysis of TMIn, apparently by reducing the concentration of H atoms, which are needed to promote the pyrolysis of TMIn.



Figure 5. 2. Pyrolysis of TMSb versus temperature in different carrier gases [57].

According to Larsen et al. [57], the decomposition of TMSb occurs via the chain reaction:

$$Sb(CH_3)_3 \rightarrow CH_3 + Sb(CH_3)_2$$
 (17)

$$CH_3 + H_2 \to CH_4 + H \tag{18}$$

$$H + Sb(CH_3)_3 \rightarrow CH_4 + Sb(CH_3)_2 \tag{19}$$

$$Sb(CH_3)_2 \rightarrow CH_3 + CH_3Sb$$
 (20)

The major challenge associated with the use of TMSb is that it leads to the incorporation of carbon as a contaminant in the epitaxial layers during the growth process.

5.1.4 TDMASb

TDMASb ([(CH₃)₂N]₃Sb) is an antimony (Sb) precursor with a relatively low vapour pressure of 0.75 Torr at 20°C, and a boiling point within the range of 50°C - 52°C [48]. It is promising for low-temperature growth of Sb compounds without the incorporation of carbon impurities. TDMASb was found to decompose at temperatures close to 360°C in the gas phase [77]. The low decomposition temperature suggests the presence of labile Sb-N bonds and the absence of a Sb-C bond [43]. The gas-phase decomposition of TDMASb molecules was described as being initiated and dominated by the homolysis reaction [77]:

$$((CH_3)_2N)_3Sb \rightarrow ((CH_3)_2N)_2Sb + (CH_3)_2N^*$$
 (21)

The dimethylaminyl radical $((CH_3)_2)N^*$ produced in this reaction can further form a hydrogen radical in the presence of H₂:

$$(CH_3)_2 N^* + H_2 \rightarrow (CH_3)_2 NH + H^*$$
 (22)

The chemistry of deposition and decomposition becomes more complicated at temperatures above 500°C and triggers the incorporation of nitrogen impurities due to the commencement of N-C bond homolysis.

5.2 Effect of V/III ratio on the morphology and size distribution of quantum dots

5.2.1 Determination of optimal growth conditions

The development of QDs entails the deposition of a strained material, usually on a lattice mismatched crystalline substrate. This step is often followed by the planar mode formation of a thin layer known as the wetting layer (WL). The planar growth of the wetting layer is interrupted at a certain critical thickness, which gives rise to the nucleation of three-dimensional (3D) nano-scale islands on top of the WL.

InSb QDs were grown on GaSb (100) 2° off substrate using both TDMASb and TMSb separately as Sb source, while TMIn was used as the source precursor for In. To determine the optimum growth conditions for growing the dot structures, an ~2.5 μ m thick calibration layer of InSb was first grown for a time of 3600 s over a range of V/III ratios between 0.8 and 4.0. Growth temperatures ranging from 300°C to 450°C were investigated for TDMASb as the Sb source, while the growth temperature was increased up to 480°C for TMSb as the Sb source. To obtain a continuous and uniform dot distribution, it is necessary for the molar flow rates of the sources to be regulated. This implies that the vapour pressures of TMIn and TDMASb should be proportional to each other. To this end, they were placed in temperature-controlled bubblers with the bubbler temperatures set at 20°C and 16°C, respectively. This amounts to each having a vapour pressure of ~1.7 Torr. However, for TMSb the bubbler temperature was reduced to - 11.5°C due to its significantly higher vapour pressure.

The surface morphologies of the epitaxial layers were examined using a Nomarski interference contrast optical microscope. The thicknesses of the epilayers were also measured using the Nomarski microscope, while more precise layer thickness measurements were carried out via cross-sectional SEM and TEM. Prior to the layer thickness measurement using the Nomarski microscope, the cleaved samples were immersed in a Murakami solution for 3 s and rinsed with deionized water before mounting it on the optical microscope. This practice helps to clearly delineate the interface between the epilayer and the substrate. Immersion in a Murakami solution for longer than 5 s yielded "blurry" interfaces due to severe etching at the layer/substrate interface. The crystallographic quality of the epilayers was evaluated by X-ray diffraction.



Figure 5. 3. Optical micrographs showing surface morphologies of InSb epitaxial layers grown on GaSb ((100)2° off towards <111>B ± 0.1°) substrate using TDMASb and TMIn.

The surface morphologies of the InSb calibration layers prior to depositing dots are shown in Figure 5.3. These layers were grown using the TDMASb/TMIn source combination. The sensitivity of the surface morphology to growth temperature and V/III ratio is clearly shown. The optimum V/III ratio varied between 1.0 and 3.2 for growth temperatures between 360°C and 425°C. The thickness, quality and the specular nature of the epitaxial layer was observed to be highly susceptible to changes in growth

parameters. The coarse surface obtained at a very low V/III ratio indicates the nucleation of defects and formation of precipitates which are typical of indium droplets, as illustrated in the SEM micrograph in Figure 5.4. Similarly, for higher values of V/III ratios (≥ 4.0) and growth temperatures $\leq 450^{\circ}$ C, the surface morphology of the samples are covered with tiny grain-like particles which are representative of antimony crystallites as seen in Figure 5.3. These crystallites are suggested in this study to be due to the high sticking coefficient of Sb, which promotes the development or nucleation of precipitates and clusters during crystal growth.



Figure 5. 4. SEM micrograph showing the surface morphology of InSb deposited at

450°C using a relatively low V/III ratio with TDMASb and TMIn as source.

Using TDMASb, temperatures above 425°C (for V/III ratios \leq 4.0) caused a deterioration of the surface. The best surface morphology (using TDMASb) was obtained using a V/III ratio of 1.0 at a growth temperature of 425°C, a result which is in agreement with Shin *et al.* [78], where TDMASb and TMIn were used for the MOVPE growth of epitaxial InSb layers at atmospheric pressure. Shin *et al.* reported that the optimum V/III ratio needed to produce a good surface morphology using a growth temperature of 425°C is approximately unity as a result of the complete decomposition of both precursors. Also, the PL spectra obtained from their study indicates a decrease in PL intensities with decreasing growth temperature, a behaviour attributed to the development of impurity emission due to degeneration of the epilayers.



Figure 5. 5. XRD patterns of InSb epitaxial layers grown on GaSb ((100)2° off towards <111>B ± 0.1°) substrates using TDMASb and TMIn.

Figure 5.5 shows the XRD patterns of InSb epitaxial layers grown on GaSb substrates using TDMASb and TMIn. The lines appearing at around $60.7^{\circ}2\theta$ represent the (0 0 4) Bragg reflections for the GaSb substrate, while the peaks at $56.7^{\circ}2\theta$ (for a V/III ratio of 1.0) and $56.8^{\circ}2\theta$ (for a V/III ratio of 2.0) are the (0 0 4) reflections from the InSb epitaxial. For a V/III ratio of 1.0, the epitaxial InSb layer is characterized by a narrower line (full width at half maximum (FWHM) value of 0.148°) compared with the epilayer that was deposited at a V/III ratio of 2.0 (FWHM ~ 0.338°). The epilayer peak for the latter sample is also slightly shifted to a larger angle ($56.8^{\circ}2\theta$). The XRD line shift and broadening can result from a number of factors, such as changes in the crystalline structure/and or phases, lattice parameter, and chemical composition. According to the XRD patterns shown in Figure 5.5, there appears to be an improvement in the crystallinity of InSb layer deposited at a V/III ratio of 1.0 as deduced from the reduced FWHM and well resolved peak. The broad and unresolved lines observed for the epitaxial InSb layer deposited at 450°C as shown in Figure 5.5 is suggested in this work to be due to factors such as lattice

relaxation and/or phase separation which can lead to the observation of new diffraction peaks in the pattern.



 $T_{g} = 300^{\circ}$ C, V/III = 0.8



 $T_g = 480^{\circ}$ C, V/III = 1.0





The optical micrographs showing the surface morphologies of epitaxial InSb layers deposited using the TMSb/TMIn source combination are displayed in Figure 5.6. Using TMSb, a decrease in growth temperature to 300°C resulted in a very rough surface and the formation of hillocks (possibly antimony crystallites) as seen in Figure 5.6. This may be due to a transformation from 2D to 3D growth due to the reduced mobility of surface adsorbed species, and partially decomposed species acting like "impurities" and promoting 3D growth. Likewise, an increase in growth temperature to 480°C and in the

V/III to 4.0 also yielded antimony crystallites. Good surface morphologies could be obtained at a growth temperature of 480°C for V/III ratios between 1.0 and 3.0.



Figure 5. 7. XRD patterns of InSb epitaxial layers grown on GaSb ((100)2° off towards <111>B ± 0.1°) substrates using TMSb and TMIn.

Figure 5.7 shows XRD patterns displaying the (0 0 4) Bragg reflections of the GaSb substrate and InSb epitaxial layers deposited at V/III ratios of 1.0 and 3.0, respectively, and using TMSb as Sb source. Both patterns contain two lines at ~60. 7° and 56.7°, resulting from the GaSb substrate and the epitaxial layers of InSb, respectively. The InSb diffraction line (for a V/III ratio of 1.0) has a FWHM of 0.127° , while the FWHM for the layer deposited at a V/III ratio of 3.0 is slightly larger (~0.139°). These values are lower than those obtained for layers deposited using TDMASb, which suggests an improved crystallinity of the InSb layers deposited using TMSb as Sb source. Similarly, the present work confirms that smooth surfaces can only be obtained for a very narrow window/range of V/III ratio when using either Sb source. Values of the V/III ratio which are not within the optimized range in general correlated with a deterioration of the surface quality due to the formation of Sb crystallites or In droplets.

5.2.2 Growth of quantum dots

Quantum dots were grown using the parameters summarised in Table 6. All the QDs were grown on a thin GaSb buffer layer with a thickness of approximately 30 to 50 nm, using a growth temperature of 425°C.

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V/	/III Ratio	TMIn Mole Fraction	TDMASb Mole Fraction	Growth Rate (nm/s)
	1	~ 5.75 x 10 ⁻⁵	~ 5.75 x 10 ⁻⁵	0.31
	2	~ 3.0 x 10 ⁻⁵	~ 6.0 x 10 ⁻⁵	0.27
	3	~ 1.93 x 10 ⁻⁵	~ 5.8 x 10 ⁻⁵	0.18



V/III = 1.0



V/III = 3.0


SEM micrographs showing the surface morphology of InSb QDs grown with various V/III ratios are presented in Figure 5.8. The dot density of the three samples grown with V/III ratios of 1.0, 2.0 and 3.0 are $\sim 1.0 \times 10^{10}$ cm⁻², 8.0 $\times 10^9$ cm⁻² and 7.0 $\times 10^9$ cm⁻², respectively (obtained using the Bruker NanoSope analysis software), which implies a reduction in dot density as the V/III ratio increases. Similarly, analysis of the images in the micrograph also showed a decrease in dot size as the V/III ratio increases. Additionally, the average dot height decreases as the V/III ratio increases, as illustrated by the SPM height histograms shown in Figure 5.9.



Figure 5. 9. SPM height histograms of GaSb substrate and InSb QDs for various V/III ratios.

The height histograms of the GaSb substrate ((100)2° off towards <111>B \pm 0.1°) and InSb/GaSb QDs grown using different V/III ratios are presented in Figure 5.9. The height histogram in Figure 5.9(a) displays a single narrow peak which is the contribution from the substrate roughness, while the other histograms are characterized by two peaks resulting from the substrate and/or buffer layer roughness and from the deposited InSb QDs. These height histograms confirm that an increase in the V/III ratio from 1.0 to 3.0

leads to a reduction in the density of the QDs, while an analysis of the diameter histograms shown in Figure 5.10 shows a change from large size to narrower size distribution with an increase in V/III ratio. The larger size distribution on the misoriented surface of a GaSb (100) substrate is ascribed to the low V/III ratio which stimulates an increase in indium species and hence causing an increase in indium adatom migration length. This leads to increased dot density and nucleation sites, and thus triggers an increase in the conversion of tiny QDs into thermodynamically more suitable larger dots via coalescence. However, as the V/III ratio increases, the number of Indium adatom available for growth on the surface reduces which automatically leads to a decrease in the migration length of indium species. Very short migration lengths can be unsuitable for nucleation and sometimes prompt a decrease in dot density. The low growth rates, shown in Table 6, were found to be beneficial for the growth of a high density of QDs using TDMASb, depending on the V/III ratio chosen. The size distribution of the dots for each sample is shown in Figure 5.10 in the form of a diameter histogram. For a V/III ratio of 1.0, the diameter of the dots ranged between 7 and 95 nm, while dot diameters of 5 - 80 nm and 5 - 47 nm were obtained for V/III ratios of 2.0 and 3.0, respectively.



Figure 5. 10. SPM diameter histograms showing size distribution of the samples in Figure 5.8.

Chapter 6

Dependence of optimum V/III ratio on substrate orientation, and influence of buffer layer on the growth of InSb quantum dots

6.1 Dependence of optimum V/III ratio on substrate orientation

The precise control of factors such as the size, stoichiometry, density and shape of QDs is vital both for optimizing the optical properties and for maximizing its applications. The exact control of these parameters is yet to be properly understood due to the stochastic process involved in the self-assembly of QDs. The primary driving force for the formation of self-assembled QDs is the strain induced by the lattice mismatch between the substrate and the deposited material [35]. This implies that explicit knowledge of both the deposited material and the substrate are vital in order to gain an adequate understanding of the formation of QDs.

The chemical kinetics of the MOVPE process are influenced by the orientation of the substrate. Similarly, the mis-orientation of the substrate by a few degrees from the surface plane plays a significant role in determining both the morphology and topography of the deposited epitaxial material. The effect of substrate orientation on the growth of InSb nanostructures by MBE has recently been reported [79]. The study was conducted on four different GaSb substrates, namely (100), (311), (411), and (511). The (411) orientation was suggested to offer a more suitable surface in MBE growth, due to the higher nanostructure density observed on this surface compared to the other orientations. To gain further insight on this subject, especially during MOVPE growth on GaSb substrates excluding the ones listed above, the effect of the GaSb substrate orientation on the MOVPE growth of InSb QDs will be discussed in this chapter.

The samples were grown simultaneously on two different GaSb substrates [(100) 2° off towards <111>B \pm 0.1° and (111) \pm 0.1°] at atmospheric pressure. TMSb was used as the Sb source. The samples were grown at a temperature of 480°C using different V/III ratios between 1.0 and 3.0.

Figure 6.1 shows 3D SPM images of the two types of substrates: (a) GaSb [(100) 2° off towards <111>B] and (b) GaSb (111). These images and other subsequent SPM images were obtained using tapping mode. Analysis of the surfaces of the GaSb substrates using the Bruker Nanoscope Analysis software gave a root mean square (rms) roughness value of 0.53 nm for the 2° off (100) substrate, compared to a rms roughness value of 0.33 nm for the (111) substrate. Both substrates were semi-insulating and epi-ready.



Figure 6. 1. 3D SPM images of the bare GaSb substrates used.

In order to study the effect of V/III ratio on dot formation, the two types of substrates were simultaneously loaded into the quartz reactor (placed side by side on the susceptor), which was subsequently purged with H₂ and annealed for 300 s before depositing a GaSb buffer layer of ~100 nm in thickness at 550°C. After a growth interruption of 120 s, the susceptor temperature was reduced to 480°C before the deposition of the InSb dots for 5 s at a growth rate of ~0.3 nm/s, using a V/III ratio of 1.0. The growth procedure was repeated two more times by varying the dot deposition V/III ratio from 1.0 to 2.0, and finally to 3.0. SPM measurements were promptly conducted on all the samples after MOVPE growth so as to prevent exposing the uncapped samples, which are susceptible to surface oxidation, for too long. Likewise, all SPM scan parameters were kept constant during measurement for consistency in all cases.



Figure 6.2. 3D SPM images of InSb dots grown simultaneously on (100) and (111)

GaSb substrates using different V/III ratios.

Figure 6.2(a) and (b) shows the 3D SPM images obtained from samples grown on both substrates with a V/III ratio of 1.0. With the aid of the Bruker NanoScope analysis software, surface features like the dot densities, heights and diameters, were deduced for the uncapped samples. Both SPM images in Figure 6.2(a) and (b) display densely spaced InSb dots. The dots which were deposited on the (100) substrate have a pyramidal shape with sharp edges, while those deposited on the (111) substrate are dome shaped. The density of the dots on each substrate was measured to be $\sim 7 \times 10^{10}$ cm⁻² and 5×10^{10} cm⁻² for the (100) and (111) substrate, respectively, while the average diameter of the dots in each case is 19 nm and 23 nm, respectively. Also, the average heights of the dots in Figure 6.2(a) and (b) were measured to be 12.6 nm and 16.3 nm, respectively. The slight increase in dot diameter and height on the (111) substrate is attributed to the coalescence of neighbouring dots on the (111) substrate. This observation is in agreement with a recent study [80] where the (111) substrate was reported to have an enhanced adatom diffusion, which results in the development of larger QDs and a simultaneous reduction in dot density as compared with the (100) substrate. This was ascribed to a larger adatom hopping barrier on the (100) substrate. Similarly, the higher dot density measured for (100) substrate signifies an increase in growth rate and enhanced decomposition of TEGa and TMIn [81] due to the presence of the atomic steps resulting from the tilt angle of the substrate.

As seen in Figures 6.2(c) and (d), an increase in V/III ratio from 1.0 to 2.0 gave rise to a slight reduction in dot density and average height on both substrates. This was accompanied by a slight increase in the measured average dot diameter as shown in Table 7. However, no significant variation in the dot distribution or arrangement was observed. A further increase in V/III ratio from 2.0 to 3.0 resulted in a significant reduction in dot density on both substrates ($\sim 4 \times 10^{10}$ cm⁻² for the (100) substrate and 7×10^9 cm⁻² for the (111) substrate). A fairly uniform dot size and shape was observed on the (100) substrate, irrespective of the V/III ratio used (for constant growth time and temperature). The morphology of the dots on the (111) substrate, on the other hand, underwent a gradual transformation from dome shaped to truncated pyramidal shaped with a flat vertex as the V/III ratio increased from 2.0 to 3.0. Also, a significant increase in dot diameter was observed on the (111) substrate for a V/III of 3.0.

The morphological transformation of the dots on the (111) substrate from dome shaped to a truncated pyramidal shaped can be explained by considering the fact that the (111) substrate offers an additional degree of freedom for the adatoms as a result of the absence of terraces induced by misorientation. This invariably gives rise to increased adsorption on the (100) substrate which can prompt a deformation or alteration of the dot morphology. Similarly, the reduction in dot density as the V/III ratio increases is attributed to the reduced number of indium adatoms available on the growth surface, which simultaneously stimulates a decrease in the migration length of indium species. Short migration lengths of the indium-species have been reported to be unsuitable for nucleation sites [82]. This was ascribed to the lack of local thickness variations (atomic steps) resulting in the formation of basically a 2D WL all through the deposition phase.

Table 7. Table summarising dot parameters obtained from SPM on samples grown or
different substrates and with different V/III ratios.

GaSb Substrate	V/III Ratio	Growth Time (s)	Average Diameter (nm)	Average Height (nm)	Density (cm ⁻²)
2°off (100)	1	5	19	12.6	~ 7×10 ¹⁰
	2		25	11	~ 6×10 ¹⁰
	3		23	10	~ 4×10 ¹⁰
	1		23	16.3	~ 5×10 ¹⁰
(111)	2	5	17	10.6	$\sim 4 \times 10^{10}$
	3		25	8.3	<7×10 ⁹

Table 7 contains a summary of results/data obtained from the SPM analysis of the images displayed in Figure 6.2. Neither substrate showed a correlation between dot diameter and the V/III ratio used for dot deposition. Strain plays a vital role in determining the height of the QDs [80]. In this study, a slight reduction in the average dot height was noticed as the V/III ratio increased. This phenomenon can be attributed to strain fluctuations resulting from the increased number of Sb which has been reported to inhibit the surface migration of atoms [80]. The trivial dependence of dot diameter on dot height indicates an uneven strain distribution on the surface of the substrates.

In conclusion, the SPM size distribution analysis of the samples shown in Figure 6.2 suggests a higher dot density for the dots grown on the (100) substrate. The misorientation on the (100) substrate is suggested to enhance the formation of surface

steps, which provides low energy growth sites and hence promotes island nucleation. Also, the presence of atomic steps on the (100) substrate can act as ledges, which provide nucleation sites. The existence of ledges/atomic steps gives rise to a larger nucleus to substrate interface, which leads to a lower total surface free energy [83]. The reduced mobility of surface adsorbed species due to the presence of atomic steps on the (100) substrate can simultaneously enhance the sticking coefficient of adatoms on the (100) surface, compared to (111) surface.

6.2 Influence of buffer layer on the growth of InSb quantum dots

Buffer layers are important in epitaxial growth and play a useful role in reducing the rms roughness of the substrate by providing an improved surface morphology that is suitable for nucleation. They may also act as a barrier which prevents impurity diffusion (e.g. of oxygen) from the substrate at high temperatures. Buffer layers can also act as strain absorbing layers [43], and are used to improve adhesion. They also accommodate the difference in lattice parameter between the substrate and the subsequently deposited material.

In order to study the effect of the buffer layer on the growth of QDs, InSb QDs were grown on GaSb ((100) 2° off towards <111>B ± 0.1°) substrates after the deposition of GaSb buffer layers with different thicknesses. The GaSb buffer layers were grown using a V/III ratio of 2.5, at a temperature of 550°C to a thickness ranging from ~50 nm to 300 nm, while the dots were deposited for 4 s at a growth temperature of 480°C using a V/III ratio of 2.0. The SPM images displayed in Figure 6.3 were obtained by varying the buffer thickness of the samples from \sim 50 nm to 300 nm. As the buffer layer thickness of the samples was increased from 50 – 250 nm, troughs/corrugations (originally absent for the bare substrate) were observed on the buffer layer surface. Deformation of this nature in heteroepitaxial growth has been ascribed [84, 85] to mechanical stress caused by lattice mismatch, while in homoepitaxial growth, surface corrugation was reported to result from kinetic epitaxial growth instabilities [86]. Another factor which can lead to a corrugated surface and faceting is surface diffusion [23]. However, the underlying physics which can be used to explain the kinetics of surface diffusion on corrugated surfaces is a stochastic process, most often described using the Markovian approximation, and the interacting single adsorbate model by the standard Langevin equation [87, 88].



Figure 6. 3. 3D SPM images showing InSb QDs grown on a GaSb buffer layer of different thickness. The substrate orientation was (100) $2^{\circ} \pm 0.1^{\circ}$ off towards <111>B.

The surface morphology of the buffer layers and the deposited dots are shown in Figure 6.3. From the SPM images, an increase in buffer layer thickness from 50 nm to ~300 nm shows the onset of surface corrugation for buffer layer thickness of ~150 nm, which persisted up to a buffer thickness of ~250 nm. The white arrows shown in Figure 6.3 (ce) indicate the alignment of successive surface troughs. It is obvious that the dots decorate these troughs and that they are aligned along them. The troughs appear to act as favourable nucleation sites for 3D islands. This can be attributed to the increased adsorption within the trough, where a high density of surface steps is expected. Analysis of the SPM images displayed in Figure 6.3 indicated that the corrugated surface has an adverse effect on the diameter and density of the deposited dots. According to the images, buffer layers with corrugated surfaces (see Figure 6.3(c-e)) led to a sparser distribution of dots with a larger diameter. During the deposition of the 300 nm thick buffer layer, a reduction in growth rate from 0.21 to 0.17 nm/s (~19% reduction) while maintaining the same value of V/III ratio and growth temperature, resulted in an even buffer layer surface as seen in Figure 6.3 (f). The absence of surface corrugation on the 300 nm thick buffer layer is suggested to be as a result of improved surface coverage of adatoms which is perhaps prompted by the reduced growth rate. The lower growth rate is presumed to induce sufficient adatom migration and strong bonding between the adsorbate atoms.



Figure 6. 4. 2D SPM image of a GaSb buffer layer with thickness ~200 nm and the corresponding height profile along the red line indicated on the SPM image.

The SPM image in Figure 6.4 is a 2D representation of the 3D image in Figure 6.3(d). The line profile on the right hand side of the figure was obtained along a line that did not intersect a 3D island. The profile typifies the "wavy nature" of the corrugated surface of this nominally 200 nm-thick buffer layer. An SPM analysis of Figure 6.4 gives a spectral rms amplitude of 3.9 nm for the corrugated surface while the image Rmax, which specifies the maximum vertical distance between the highest and lowest data points in the image was deduced to be 24.9 nm. The average width of the terraces on the corrugated surfaces is measured to be within the range of 200 – 500 nm. The large value of terrace width is significantly greater than the terrace length/width expected for a $2^{\circ} \pm 0.1^{\circ}$ misorientation, indicating multi-monolayer step formation.



Figure 6. 5. Plots of (a) dot density and (b) dot diameter, as a function of buffer layer thicknesses respectively.

Figure 6.5 shows plots of dot densities and diameters as a function of buffer layer thickness. From the plots, it is clear that an increase in buffer thickness from 50 – 250 nm gives rise to a gradual reduction in dot density, accompanied by an increase in diameter of the dots, while a buffer thickness of 300 nm resulted in a substantial increase in dot density which was accompanied by a reduction in the dot diameter. This makes the result an "outlier" in the plots shown in Figure 6.5. The decrease in dot density which was observed on the corrugated surface is suggested to be due to the low surface free energy which induces a reduction in adsorption energy on the corrugated surface.

It is interesting to note that the shapes of the dots grown on a GaSb buffer layer with thickness ranging from 150 – 250 nm were truncated pyramids with flat vertices (see Figure 6.6), unlike those grown on the thinner buffer layers (50 – 100 nm), which were almost dome shaped. The truncated vertex can result from surface relaxation [89], and can also be induced by the energetics of the SK growth mode [90] which can alter the dot morphology. Furthermore, the effect of surface relaxation can also account for the increased dot diameter on the corrugated surfaces (buffer thickness 150 – 250 nm).



Figure 6. 6. SPM image of InSb dots grown at 480°C and a V/III ratio of 2.0 on a GaSb buffer layer of thickness ~150 nm showing truncated coned shaped dots.

In conclusion, corrugated buffer surfaces was observed to introduce order in the arrangement of the dots, which formed preferentially inside the troughs. The shape and size of the dots were observed to be sensitive to the thickness of the buffer layer, the deposition of a thin (\sim 50 – 100 nm) GaSb buffer layer and the reduction in growth rate during the deposition of the 300 nm thick buffer have been established to provide a suitable surface for the formation of uniformly spaced dots with a high areal density. However, no correlation was observed between buffer layer thickness and the height of the dots.

Chapter 7

Growth and photoluminescence characterisation of single layer InSb/GaSb quantum dot structures

7.1 Properties of samples deposited and growth details

Each sample presented in this chapter was grown on a GaSb substrate ((100) $2^{\circ} \pm 0.1^{\circ}$ off towards <111>B). Uncapped structures were deposited prior to the growth of the capped samples using similar growth conditions. This precautionary step was adopted so as to establish the presence of the dots before capping, and to establish that the size and dimensions of the dot parameters were identical for each structure.



Figure 7. 1. Schematic cross-section of the intended sample (sample 1).

The schematic cross-section of the intended sample (denoted as sample 1) is shown in Figure 7.1: a 300 nm thick GaSb buffer layer was deposited onto a GaSb substrate using a V/III ratio of 2.0, and InSb QDs were subsequently grown on the buffer. A 200 nm GaSb cap was then deposited using a V/III ratio of 6.0. The GaSb buffer layer was deposited at a susceptor temperature of 550°C and a growth rate of ~0.17 nm/s. The buffer layer was grown immediately after annealing of the substrate. Details of the preliminary sample preparation and growth procedure were discussed in sections 4.2 and 4.3, respectively. The susceptor temperature was reduced to 480°C after the growth of the buffer layer, and InSb dots were deposited for 5 seconds at a V/III ratio of 2.5 at a growth rate of ~0.35 nm/s, which was determined from the growth rate established for a 2.5 μ m-thick calibration layer. This step was followed by the termination of the metalorganic flow

through the reactor for 120 seconds at 480°C. The growth interruption in this context is known as a "ripening time", a measure deemed necessary to allow the deposited dots to stabilise after formation. Finally, a 200 nm GaSb capping layer was grown at a final susceptor temperature of 510°C and a nominal growth rate of ~0.05 nm/s.

7.2 SPM analysis of uncapped samples

All uncapped samples were analysed with the SPM system described in section 4.4.2 using the tapping mode technique. This procedure was adopted because it has been established to be more stable and sensitive to variations in both amplitude and phase of the cantilever oscillation. Tapping mode operation also has an enhanced lateral resolution compared to contact mode.



Figure 7.2. SPM images of (a) plain substrate, (b) uncapped InSb dots deposited directly on the substrate, (c) GaSb buffer layer, and (d) uncapped InSb dots on a GaSb buffer.

The SPM images of the bare GaSb substrate used, the uncapped dots deposited on the bare substrate without a buffer layer, the GaSb buffer and the uncapped InSb dots on a buffer layer are shown in Figure 7.2. Information such as dot density, diameter, height, and size distribution were extracted from the samples using the Bruker NanoScope analysis software (version 1.40), by applying a suitable fitting technique to the height histograms.



Figure 7.3. Height histograms of uncapped InSb dots grown (a) directly on the substrate and (c) on a buffer layer. Least squares fits to the height histograms are shown in (b) and (d), respectively.

The histograms in Figures 7.3(a) and (c) were fitted using Origin 8.5 and the best fits are shown in Figures 7.3(b) and (d), respectively. The fitting procedure chosen for the height histograms was used to extrapolate their threshold height values, which were determined to be 8.3 nm and 8.5 nm for the uncapped samples in Figure 7.2(b) and (d),

respectively. The average dot densities were $\sim 3.6 \times 10^{10}$ cm⁻² and 5.0 × 10¹⁰ cm⁻², respectively, which were deduced for all features having heights above these threshold values. The narrow, sharp peaks present in the histograms are ascribed to contributions from the substrate roughness or buffer layer roughness, whereas the broader peak in each height histogram is attributed to the QDs. This is supported by the absence of the broader peak in the histogram of the bare substrate (refer to Figure 5.9(a)). Further analysis of the height histograms showed that in both cases most of the dots have heights in the range of 7.5 - 15.8 nm.



Figure 7.4. Size distribution histograms of uncapped InSb dots deposited on (a) a bare GaSb substrate, and (b) a GaSb buffer layer.

The respective dot diameter distributions are shown in the form of size distribution histograms in Figure 7.4. The histogram in Figure 7.4(a) shows that the dot diameters are between 5 nm and 30 nm, with most of the dots having diameters below 25 nm. A similar trend is observed for the histogram in Figure 7.4(b). However, a small number of islands with larger diameters (\sim 35 – 50 nm) are observed in both histograms, which is attributed to the high areal density of the dots, which leads to coalescence. To summarise, when InSb growth took place directly on the substrate, the dot density and heights differed slightly from those grown on a GaSb buffer layer, despite the use of nominally identical InSb deposition conditions. This is ascribed to a higher number of nucleation sites on the buffer layer. This is confirmed by the increased rms roughness of the buffer layer (0.828

nm) compared to that of the bare substrate (0.525 nm) [91]. The surface roughness of the GaSb buffer was determined using a conventional SPM line scan technique.



Figure 7. 5. (a) 2D SPM image of GaSb buffer surface with corresponding roughness spectrum (taken at the position of the green line in (a)). (b) SPM image of uncapped InSb dots on GaSb buffer after annealing at 510°C.

The green line on the SPM image in Figure 7.5(a) depicts the position where the line scan for the roughness spectrum was taken. This study suggests that the increased rms roughness of the buffer increases the number of nucleation sites and hence a higher areal dot density. Figure 7.5(b) is a 3D SPM image of the uncapped dots grown on a buffer and subsequently annealed for 3600 seconds at 510°C in a hydrogen ambience. No significant change was noticed between the SPM images in Figure 7.2(d) (for a similar sample, but as-grown) and Figure 7.5(b). This annealing experiment was performed to shed light on results presented in sections 7.3 and 7.4 where the effect of capping the dots at a final temperature of 510°C is discussed.

7.3 PL analysis of the capped sample

PL measurements were performed on the samples in order to determine the nature of the optical transitions within the samples. The spectra in Figure 7.6 were collected from the capped InSb dot sample, henceforth denoted as sample 1 (a schematic cross-section is shown in Figure 7.1), the GaSb substrate and the substrate plus buffer layer, at a temperature of 10 K. The growth conditions and procedure for these samples are similar to those mentioned in sections 4.3 and 7.1.



Figure 7.6. 10 K PL spectra of capped sample containing InSb dots (sample 1), GaSb substrate, and substrate with buffer layer.

The uncapped samples did not emit PL, except for emissions which are known to be typical of the substrate used. This is ascribed to strong surface recombination in the uncappped dots. The presence of the capping layer is thought to induce strain in the embedded QDs, which simultaneously improves the mobility of the carriers at the interface between the buffer and the cap layer. Apart from protecting the QDs from exposure to ambient conditions and avoiding oxidation by shielding the dots from the atmosphere, the cap layer is fundamental in tailoring the band gaps and/or altering the atomic arrangement of the QDs, which determines device performance such as

luminescence. However, inter-diffusion between the first monolayer (ML) of the capping material and the underlying layer often occurs during the capping process [92].

The spectrum from capped sample 1 is distinguished by four prominent PL lines at 796 meV, 777 meV, 770 meV and 736 meV. The line at 796 meV has a FWHM of \sim 3.5 meV and is attributed to bound exciton recombination (BE₄), while the free electron-to-native-acceptor transition or donor-native acceptor transitions (A-line) [93] [94] is assigned to the 777 meV line, with a FWHM of \sim 5.8 meV. These lines (BE₄ and A-lines) are known to originate from the GaSb substrate. The other two lower energy lines at 770 meV and 736 meV are ascribed to the A-line in the epitaxial GaSb and emission from the epitaxial InSb, respectively. These lines are absent in the substrate material and are believed to originate from the epitaxial materials deposited.



7.3.1 Temperature dependent PL measurement of capped sample and substrate

Figure 7.7. Temperature dependent (semi-log plot) PL spectra of sample 1 and 10 K PL spectrum of the GaSb substrate.

The temperature dependent PL spectra obtained from sample 1 are shown in Figure 7.7, together with the 10 K PL spectrum of the GaSb substrate. With reference to the PL of sample 1, the 770 meV line, which has a FWHM of ~9.8 meV, is suggested to be the A-line in the epitaxial GaSb, red-shifted due to strong compensation effects (potential fluctuations [95]) in these layers that were grown at relatively low (non-ideal)

temperatures [91]. The temperature dependent measurements revealed that the 770 meV line is unstable and disappear at ~60 K, as shown in Figure 7.7. According to a previous report [35], the energy line at 770 meV was designated the I-line and was confirmed to emerge after the inclusion of an InSb containing layer within a GaSb matrix. An increase in the average thickness of the InSb deposited was reported to induce a long wavelength shift and an increase in the FWHM. This behaviour was described to be resulting from radiative recombination of excitons in quasi-2D InSb islands.



Figure 7. 8. Temperature dependent PL spectra of GaSb buffer layer deposited on GaSb substrate.

Figure 7.8 shows temperature-dependent PL spectra obtained at 10, 40 and 60 K for the epitaxial GaSb buffer layer. The A-line, which is red-shifted and thus appears at 770 meV, exhibits the same behaviour as the line at 770 meV in sample 1. This line rapidly disappears at ~60 K, as can be seen in the figure. The A-line from the substrate (at 777 meV) increases strongly at higher temperatures. This behaviour confirms that the 770 meV line from sample 1 originates from the GaSb buffer layer. The dominance of the substrate luminescence as the temperature increases is due to an enhancement in the radiative recombination of native defects through the A-line.

The peak at 736 meV from sample 1 (FWHM of \sim 16 meV) exhibited peculiar characteristics at different temperatures, as shown in Figure 7.9. Emission at this energy has been ascribed to emission from InSb QDs [6] [7] [8]. A substantial reduction in the

intensity of this line is noticed as the temperature increases above 50 K, while the emission vanishes completely at 80 K. The strong reduction in intensity of this line is accompanied by line broadening and a slight blue shift at 20 K, while a small red shift is observed as the temperature is further increased to 60 K.



Figure 7.9. Temperature dependent PL spectrum (semi-log plot) of the energy line at 736 meV.

These attributes are comparable to what was reported by Lyublinskaya *et al.* [96] for capped InSb QDs, where a blue shift was observed as the temperature increased from 20 to 100 K. The blue shift was ascribed to a redistribution of localised carriers in the dots at elevated temperatures, which coincidentally activates the population of states with lower confinement energies. With a further increase in temperature, the blue shift becomes saturated and consequently, the simultaneous red shift from the renormalisation of the energy gap, became dominant.

7.3.2 Excitation power dependent PL measurement of capped sample

The lowest energy line at 736 meV is excitation power dependent and was observed to shift to higher energies and broaden as the excitation power was increased. The shifting followed a systematic trend, while the other peaks remained energetically at the same position as shown in Figures 7.10(a) and (b). All the excitation power dependent PL measurements for sample 1 were carried out at a constant temperature of 10 K. The magnitude of the apparent shift in energy position differed slightly (between ~6 – 8 meV)

for different positions of the excitation spot on the sample. A similar trend was noticed when using different apertures sizes in the adjustable iris diaphragm, which is used in the PL system to adjust the excitation spot size on the sample.



Figure 7. 10. (a) Normalised 10 K PL spectra of sample 1 as a function of excitation power. The behaviour of the low energy PL peak with laser power is shown in more detail in (b). (c) Peak position of the low energy PL line versus laser power. (d) FWHM of the low energy line versus excitation power.

The normalised PL spectra of sample 1 (schematically represented in Figure 7.1) as a function of laser power are shown in Figure 7.10(a) and (b), while Figure 7.9(c) quantifies

the position of the low energy line in Figure 7.10(b) as a function of excitation power. An increase in FWHM was accompanied by a strong blue shift of ~10 meV (from 732 meV to 742 meV), as displayed in Figures 7.10(b) and (c). The blue shift exhibited by the capped sample is a characteristic that is usually ascribed to a type-II band alignment and is similar to that reported in [37], where this behaviour was attributed to transitions within InSb QDs. Alternatively, the average energy of these transitions is determined by the stable populations of the QD energy state distribution induced by either high intensity or temperature, and the preferential population of larger dots (which offer lower energy states) at low temperature. Thus most of the carriers will be confined in the larger dots at low temperature and low laser power due to their low energy states, but as the laser power increases, carriers are expected to progressively populate the smaller dots, thereby generating a shift towards higher energies [91]. The dependence of the FWHM on excitation power for this peak is shown in Figure 7.10(d). For the lowest excitation power (2 mW) the FWHM was measured to be ~13 meV and this increased non-linearly to ~25 meV as the excitation power was raised to 133 mW, as shown in Figure 7.10(d).

7.3.3 Effect of source mole fraction on PL spectra of capped samples

The effect of growth rate on the PL emission of capped InSb dot structures was studied by varying the total mole fraction (TMIn + TMSb), while keeping the V/III ratio constant, for two different samples (A and B). The growth conditions and structures for both samples were similar to those used for sample 1 described in Figure 7.1. The only difference was that the dots in samples A and B were deposited for a growth time of 4 seconds. Prior to capping samples A and B, reference SPM samples (uncapped) were deposited using identical growth conditions to the capped samples. The summary of parameters varied for the uncapped samples, and their respective properties as determined using SPM, are summarised in Table 8.

Table 8. Summary of sample properties and parameters varied during growth

Sample Name	Average Diameter (nm)	Average Height (nm)	Dot Density (cm ⁻²)	TMIn Mole Fraction	TMSb Mole Fraction	Total Mole Fraction (TMIn + TMSb)
Α	13.8	6.75	$\sim 4.3 \times 10^{10}$	4.60 x 10 ⁻⁵	1.15 x 10-4	1.61 x 10-4
В	17.5	8.25	$\sim 3.3 \times 10^{10}$	5.45 x 10 ⁻⁵	1.35 x 10 ⁻⁴	1.90 x 10 ⁻⁴

It is seen in Table 8 that an increase in total mole fraction gives rise to a decrease in dot density, while the average dot diameter and height increased. The decrease in dot density as the total mole fraction increases could be due to the coalescence of the dots in sample B as a result of their large size distribution. This phenomenon can be ascribed to a higher growth rate of the islands when the total mole fraction was increased, which simultaneously gave rise to a decrease in migration length of In and Sb species. Both samples were subsequently capped with a GaSb layer of ~200 nm, and the PL spectra obtained is shown in Figure 7. 11.



Figure 7. 11. Normalised 10 K PL spectra of capped sample A and B containing InSb QDs deposited at different growth rates.

The PL spectra in Figure 7.11 were obtained from the bare GaSb substrate and the capped samples (A and B). The low energy lines appear at ~750 meV (FWHM ~25 meV) and 730 meV (FWHM ~15 meV) for samples A and B, respectively. This behaviour is similar to that reported by Alphandery *et al.* [6] for InSb dots embedded in a GaSb matrix, where the growth temperatures and deposition times were varied and optimised so as to achieve the highest PL peak intensities. Alphandery *et al.* initially observed a PL peak at ~770 meV for a growth time of 1 second, which was ascribed to the WL. An energy line appearing at ~735 meV, which was attributed to the QDs, was subsequently observed by these authors as the growth time increased from 1 to 2 seconds. The low energy line appearing at ~735 meV abruptly dominated the spectrum and red shifted to ~715 meV

as the deposition time was further increased to 5 seconds. The present study suggests that the change in the low energy PL peak intensities (at ~750 and 730 meV) for the capped samples can occur as a result of the effect of quantum confinement, and this is supported by the SPM analysis, which shows that the dots in sample A have a smaller average diameter compared to sample B. Similarly, the increased FWHM measured for sample A might be due to its higher mean dot density and may also indicate a bimodal size distribution for the dots in the sample. However, as the growth time for sample B was increased from 4 to 5 seconds while keeping the mole fraction constant, an abrupt drop in the PL peak intensity of the low energy line was noticed, as can be seen in Figure 7.12.



Figure 7. 12. (a) Normalised 10 K PL spectra (semi-log plot) of capped sample B showing behaviour as growth time increase. (b) Linear plot of the low energy peak in (a).

The optical behaviour of sample B for two different dot deposition times is displayed in Figure 7.12. The spectra show a sudden reduction in the intensity of the low energy line as the growth time increases. This behaviour has also been observed by Alphandery *et al.* [6] and was ascribed to the onset of the formation of dislocations. This anomaly is simultaneously accompanied by a red shift of the low energy PL line, since the dots are expected to become larger and hence stimulating a decrease in the confinement energy.

7.3.4 Thermal quenching of the low energy PL in the single layer InSb/GaSb capped sample

The thermal activation energy for the quenching of emission from the low energy PL line of sample 1 (see Figure 7.6) was extracted using PeakFit software (version 4.12). Due to significant overlap between the low energy PL and emission at higher energy, the temperature dependent Pl spectra was systematically fitted to extract the integrated emission intensity (semi-log plot in Figure 7.7). Each single peak was assumed to be a convolution of Gaussian and Lorentzian functions, and the smoothing technique chosen utilised a fast Fourier transform (FFT) filter algorithm, such that the primary data stream was not modified. An illustration of the data fitting technique applied in computing the thermal activation energies for the quenching of emission with temperature is shown in Figure 7.13.



Figure 7. 13. Demonstration of data-fitting procedure used in studying the temperature dependent PL spectra for the capped sample described in section 7.3: (a) 10 K spectrum, (b) 50 K spectrum.

It is clear from Figure 7.13(a) that six distinct PL peaks were fitted. Peak 1, at \sim 736 meV, is believed to be emission from the epitaxial InSb, since it is absent in the PL spectrum of the GaSb substrate used, as illustrated in Figure 7.7. The phonon replicum of the A-line (A-LO) at \sim 748 meV is represented by peak 2, while peak 3 at \sim 770 meV, is the A-line

from the epitaxial GaSb. Peak 4 at 779 meV represents the donor-native acceptor and/or free electron-to-native-acceptor transitions (A-line) from the GaSb substrate, peak 5 at 796 meV represents bound exciton recombination (BE₄), and peak 6 at 800 meV represents the E-line [93] [94] [95].

Throughout the fitting process, it is necessary to fix the width of peaks 2 (A-LO) and 4 (A-line) due to the fact that peak 2 is a phonon replicum of peak 4. At lower temperatures, the fitting of the A-line was tricky due to the presence of overlapping peaks; a reasonable fit could only be obtained by assuming that the peaks have both Gaussian and Lorentzian characteristics. As the temperature increased peak 3, which is the A-line from the epitaxial GaSb layer, became considerably weaker, as shown in Figure 7.13(b), and disappeared completely at \sim 60 K. The disappearance of peak 3 at \sim 60 K gives rise to a broadening of the A-line in peak 4 due to thermal effects, thereby inducing the A-line to assume a Gaussian character. An abrupt thermal quenching of peak 5 (BE₄) at 20 K was observed, while a blue shift of the E-line (~0.8 meV) at temperature of 50 K, which is simultaneously accompanied by a decrease in its intensity, was noticed as shown in Figure 7.13(b). The thermal quenching of BE₄, and the blue shift of the E-line accompanied by a reduction in its PL intensity as the temperature increases, are in good agreement with previous reports for GaSb [95] [97]. Generally, knowledge of the optical properties and/or behaviour of the GaSb substrate as a function of temperature is beneficial towards achieving a proper fitting of the energy peaks.

Figure 7.14 is an Arrhenius plot of the integrated intensity of the low energy peak obtained for sample 1. The values used for the Arrhenius plot were deduced coherently by measuring the logarithmic intensity value of the low energy fitting (peak 1) for each temperature-dependent PL spectrum respectively.



Figure 7. 14. Arrhenius plot of the integrated intensity of the low energy PL of sample 1. The equation used to describe the thermal activation energy of the luminescence

quenching was [98] :

$$I = \frac{I_0}{\left[1 + C \exp\left(\frac{E_a}{kT}\right)\right]}$$
(23)

where I_0 is the initial intensity obtained at low temperature. The coefficient *C* is normally assumed to be temperature independent and is extracted from the temperature where the emission starts to quench (i.e. it corresponds to the "knee" in the Arrhenius plot [91]). Equation (23) was fitted [98] to the data in Figure 7.14 and the thermal activation energy for this transition was determined to be $E_a = 37.1 \pm 5.4$ meV. The low value of the activation energy is contradictory to the typical behaviour of the emission from QDs, which can often be detected up to room temperature.

7.4 TEM analysis

The acquisition of in-depth information with respect to the structural properties of the capped sample (such as the shape, size, arrangement of the QDs, chemical composition, structural deformation of the lattice and possible formation of defects), was carried out using various conventional transmission electron microscopy (CTEM) modes, including bright-field (BF) and dark-field (DF) imaging conditions. During this process, it is

imperative that all original samples are adequately thinned using a destructive preparation process so that there is substantial interaction between the incident beam of electrons and the atoms from the samples. Information regarding the chemical composition of the thinned area of the samples investigated was determined using energy dispersive X-ray spectroscopy (EDS).



Figure 7.15. Dark-field cross-sectional TEM micrograph of sample 1. The red line indicates the position of an EDS line scan (a schematic cross-section of sample from Figure 7.1 is repeated here).

The TEM micrograph in Figure 7.15 is a dark-field image of sample 1, which nominally contains a single layer of InSb QDs buried between the GaSb buffer and capping layers. The schematic cross-section for this sample (from Figure 7.1) has also been reproduced here.

The micrograph reveals a QW with a thickness of ~10 nm, rather than contrast from QDs. No clear confirmation of extended defects or the presence of QDs between the buffer and cap layers was found, even though SPM images clearly showed QD formation on the uncapped sample – see Figures 7.2 (b) and (d). This suggests that the absence of QDs in the capped sample may occur as a result of inter-diffusion of gallium (Ga) and indium (In) during the deposition of the cap layer, giving rise to a QW instead of QDs [91]. Besides inducing inter-diffusion, which has been reported [92] to possibly occur during the capping process, capping-induced strain can potentially alter the surface of the material and can modify the film/island morphology during epitaxial growth [99] [100] [101].



Figure 7. 16. Quantified EDS line scan across the interface between the GaSb buffer and cap layers taken for the micrograph in Figure 7.15.

Figure 7.16 contains the quantified EDS line scan data/chemical composition, which was obtained from sample 1 at the position indicated by the red line in Figure 7.15. The interfaces between the QW and the GaSb cap and buffer layers are indicated by the two white dashed lines. The line scan confirms the presence of a thin InGaSb layer with $\sim 17\%$ indium on the group III sub-lattice. However, the presence of Ga at the interface where only InSb was expected, suggests the occurrence of inter-diffusion. This may be induced by strain inhomogeneities which will enhance inter-diffusion during the deposition of the cap layer, bearing in mind that the cap layer was deposited at a slightly higher temperature than the QD material.

7.5 Band edge simulation using Nextnanomat software

To acquire more knowledge about the expected attributes of the samples grown in this study, the results obtained from TEM analysis and self-consistent Schrodinger-Poisson-calculations were used to model and simulate the energy levels and wave functions for a 1D band alignment representation of the samples. All simulations were carried out using Nextnanomat software (version 3.1.0.0).

Sample 1 was modelled as a ~10 nm thick $In_{1 - x}Ga_xSb$ QW, sandwiched between a 300 nm GaSb buffer layer and a 200 nm GaSb capping layer. A lattice temperature of 10 K and an estimated Ga mole fraction of 0.82 < x < 0.84 (deduced from the quantified EDS line scan) was used for the alloy composition. In addition, homogeneous strain was assumed. The software also assumes a 50:50 split of the band gap discontinuity between the conduction and valence bands of the two materials [91].



Figure 7. 17. Simulated representation of band alignment, wave functions and energy levels for a 10 nm In_{0.17}Ga_{0.83}Sb/GaSb QW structure.

Figure 7.17 presents the simulation results for sample 1, for which a QW structure was assumed. The modelled result shows a type-I band alignment, while the estimated values of the ground state energy levels for the electron and heavy hole are 718 meV and –20 meV, respectively. A 738 meV energy difference was thus determined for the transition of an electron to the ground state for the heavy hole. This value is in good agreement with the data collected from the PL spectrum for sample 1.

Chapter 8

Growth and photoluminescence characterisation of double layer InSb/GaSb quantum dot structures

8.1 Growth details and properties of double layer InSb/GaSb quantum dot structures



Figure 8.1. Schematic cross-section of the intended double layer InSb dot sample (sample 2).

The schematic cross-section of the intended sample (referred to as sample 2) is presented in Figure 8.1. The structure consists of an epitaxial stack of two InSb QD layers, separated by a 30 nm thick GaSb "spacer" layer, and deposited on a GaSb buffer layer (~300 nm thickness), using a GaSb substrate (2° off <100> towards <111>B). The growth procedure and sequence is similar to that previously discussed in section 7.1 for sample 1, but with slight changes in some growth parameters. The InSb dots were deposited at a slightly lower nominal growth rate of ~0.27 nm/s compared with the single layer InSb/GaSb structure discussed in section 7.1, while the GaSb capping layer (~200 nm) and the spacer were both deposited at a growth temperature of 500°C. However, the InSb growth temperature was maintained at 480°C and the deposition time was 5 seconds for each layer.

The low nominal growth rate was established to be favourable for obtaining a high dot density with an appropriate V/III ratio and growth temperature. This was determined by the growth and thorough analysis of several series of thick calibration layers prior to the deposition of the buffer, dot and cap layers. Furthermore, the steps on the mis-oriented

substrate promoted adsorption, resulting in a reduction in the surface diffusion length of the indium species during deposition, which accounts for the high dot density measured for the uncapped sample 2 [102]. An SPM image of sample 2 (without a cap), which was used as a reference sample for SPM is shown in Figure 8.2(a). The dots and GaSb buffer in this sample were deposited using similar growth conditions as the capped sample 2 shown in Figure 8.1. Analysis of this SPM image revealed a slightly lower dot density of \sim 4.3 × 10¹⁰ cm⁻² than was observed for the uncapped single layer dot structure (grown on a buffer) described in section 7.1, which had a dot density of \sim 5.0 × 10¹⁰ cm⁻². This difference in dot density is anticipated, since the QDs were deposited at slightly different growth rates, as mentioned earlier. The average dot densities obtained for the uncapped samples in this work are comparable with the value reported recently for InSb/GaSb QDs grown by MBE [103].



Figure 8.2. (a) SPM image of the uncapped reference sample (b) Diameter histogram of uncapped dots in (a).

The size distribution histogram in Figure 8.2(b) shows that the majority of the uncapped dots have diameters between 5 and 32 nm, while the height image in Figure 8.2(a) shows evidence of dot coalescence, which have been circled in green. This study suggests that the low growth rate, which was found to be beneficial for realizing high dot densities, may trigger the onset of Ostwald ripening [104], subsequently giving rise to coalescence. No remarkable changes in dot height were observed compared with the dots described in section 7.1.

8.2 PL analysis of capped double layer InSb/GaSb quantum dot structure.



Figure 8.3. Normalised low temperature PL spectra of the GaSb substrate, sample 1 and sample 2.

Figure 8.3 presents the normalised low temperature PL spectra for the GaSb substrate, sample 1 (discussed in section 7.1) and sample 2, which have been plotted on same axis for easy comparison. The spectral was acquired at an excitation power of 55 mW and a temperature of 10 K. Peaks arising from the GaSb substrate are clearly differentiated from the epitaxial material. The low energy emission lines (~736 meV and 740 meV) measured from the normalised low temperature PL spectra for samples 1 and 2, respectively, are very similar to that reported for strained Ga1-xInSb/GaSb (x ~15%) single QWs (733 meV) grown by MOVPE [105]. Furthermore, there was no clear splitting of the low energy PL emission lines observed in either sample.

The PL spectrum obtained from sample 2 is comparable to that obtained from sample 1, but with a few observable differences. One difference in the PL spectrum from sample 2 is the increase in strength of its low energy PL emission line (from epitaxial InSb) compared to that of sample 1. This is attributed to the fact that sample 2 contains two layers of InSb, while sample 1 only has one layer. However, some authors [39] have

proposed that the insertion of a thin GaSb spacer improves the crystal quality of subsequently grown InSb; this effect could contribute to the stronger PL emission of sample 2 [102]. The slight mismatch in the low energy emission lines for the two samples (~736 meV for sample 1 and ~740 meV for sample 2) is ascribed to the differences in their confinement energies, as they were grown at slightly different growth rates and capping temperatures. The absence of the A-line from the epitaxial GaSb (observed at ~770 meV) in sample 2, which was present in sample 1, is attributed to the enhanced efficiency of the InSb embedded layers at capturing photo-excited carriers which gives rise to weak recombination in the poor quality epitaxial GaSb layers grown at relatively reduced temperatures. The successive changes in the thickness of the deposited InSb can stimulate inhomogeneities in the width and barrier height of the island. This ultimately gives rise to different ground state confined energy levels, which invariably alters the recombination energy. Also, for the same excitation power (~55 mW), the FWHM of sample 2 (~20 meV) was greater than that of sample 1 (~16 meV).





Figure 8.4. Normalised 10 K laser power dependent PL spectra of sample 2 showing the behaviour of the low energy PL peak.

Figure 8.4 presents PL spectra for sample 2 collected at 10 K and laser powers of 2.5 mW and 105 mW. The results were normalised to show clearly the behaviour of the

low energy PL peak. A slight blue shift (\sim 4 meV) in the low energy peak at \sim 740 meV was noticed as the excitation power increased. This behaviour is similar to that observed for sample 1 and is ascribed to the progressive filling of higher lying states before recombination. However, the broadening of the low energy emission line and the blue shift observed for sample 2 is considerably smaller than that observed for sample 1, where a blue shift of \sim 8 meV was established.

The reduced blue shift and broadening of the low energy PL line for sample 2 with increasing laser power is suggested to result from the insertion of the GaSb spacer, which is believed to enhance the quality of the InSb layer by improving the interface on which the subsequent layer (where the dots are buried) nucleates. This therefore improves the epitaxial growth of more uniform layers in terms of thickness fluctuations and composition.



Figure 8.5. (a) Temperature dependent PL spectra (semi-log plot) of the PL line at 740 meV for sample 2. (b) Arrhenius plot of the integrated PL intensity for both samples 1 and 2.

Figure 8.5(a) presents a semi-log plot of the low energy PL peak observed for sample 2, collected at various temperatures. This emission was detected up to 80 K. The quenching of the luminescence with increasing temperature is accompanied by a red shift and narrowing of the PL line. This behaviour is perhaps due to the redistribution of carriers caused by the domination of recombination in weakly confined regions, which marks the
onset of non-radiative recombination processes. The decrease in luminescence as temperature increases is suggested to result from the dissociation of excitons and the thermal activation of competing non-radiative recombination channels [102]. Arrhenius plots of integrated PL intensity of the low energy lines for both samples 1 and 2 are shown in Figure 8.5(b) for easy comparison. A lower value of the thermal activation energy, $E_a = 11.7 \pm 1.0$ meV, was determined for sample 2 using a similar procedure to that described in section 7.3.4 for sample 1 ($E_a = 37.1 \pm 5.4$ meV). This unusual fast quenching of the low energy emission is ascribed to the capture of carriers by defect centres. The lower activation energy deduced for sample 2 compared with sample 1 also suggests a probable occurrence of intermixing at the interface.

8.3 TEM analysis of capped double layer InSb/GaSb quantum dot structure.



Figure 8.6. (a) Dark-field cross-sectional TEM micrograph of sample 2. (b) Magnified cross-sectional TEM micrograph of (a). *INSET*: schematic cross-section for sample 2 (from Figure 8.1).

Figure 8.6 is a dark-field cross-sectional TEM micrograph obtained from sample 2. The TEM micrographs shown in Figures 8.6(a) and (b) provide no evidence for the existence of InSb dots, but rather display two QWs of $\sim 8 - 9$ nm in thickness. The quasi two-

dimensional layers which represent the QW are distinguished from the surrounding GaSb matrix by the two bright lines at the interface where the QDs were expected.

A minor deviation was observed between the nominal and measured growth rates (larger by $\sim 10\%$) for the buffer layer from the TEM micrographs. This variation is ascribed to variations in growth rates which are instigated by the improved decomposition of TMSb molecules at high temperatures. The white contrast in the forms of spots which are distributed across the TEM micrographs is attributed to mechanically induced artefacts resulting from damage during ion beam thinning.



Figure 8.7. Bright-field cross-sectional TEM micrograph of sample 2 showing a threading dislocation. The DF image is shown in Figure 8.6(b).

The TEM micrograph shown in Figure 8.7 is a BF cross-sectional TEM micrograph version of the DF micrograph shown in Figure 8.6(b). A disruption in the periodic lattice of the material, highlighted by arrows in the micrograph, is observed. The disruption seems to originate from the substrate and is known as a threading dislocation. The dislocation is observed to thread through the spacer layer and into the capping layer. It is suggested that this threading dislocation has been caused by misfit induced by structural relaxation in the growth layer.

8.4 Simulation of the effect of spacer layer thickness on the band edge emission and energy levels of InGaSb/GaSb quantum wells

Changes in the spacer thickness are expected to create significant modifications in the electronic and optical properties of quantum structures. These modifications may vary for different structures. A thin spacer can increase the mobility of electrons by moderately restraining electron scattering, while a thick spacer can give rise to a reduction in the electron mobility. Likewise, a spacer can also induce a decrease in the electrostatic potential for the confined electrons at the interface [106]. To gain more insight into the electronic properties of the samples with more than one InSb layer separated by GaSb spacers (such as sample 2), it is crucial to understand how different spacer layer thicknesses affect these structures. Therefore, the effect of spacer thickness on the optical properties of sample 2 was investigated via simulation using the nextnanomat software, while some of the values used were extrapolated coherently from the TEM data in Figure 8.6. However, sample 2 was modelled as a double In_{0.17}Ga_{0.83}Sb QW of thicknesses ~9 nm. The results of this modelling are shown in Figure 8.8.



Figure 8.8. Modelled representation of the band alignment showing the wave functions and energy levels for 9 nm InGaSb/GaSb QWs separated by (a) a thin (4 nm) GaSb spacer, and (b) a thick (30 nm) GaSb spacer.

Using the self-consistent Schrodinger-Poisson-current calculation and the effective-mass quantum model for holes and electrons, an interaction of the energy levels between the localized eigenstates in the QWs was noticed as the GaSb spacer thickness decreased to 4 nm, with one eigenstate having a higher energy than the other as shown in Figure 8.8(a). A weak coupling between the electron eigenstates (e1, e2) within the conduction band was also observed.

For a spacer layer thickness of 30 nm, as shown in Figure 8.8(b), the electron eigenstates (e1, e2) within the conduction band, and the ground state wave function for the heavy holes (hh1, hh2) in the valence band in both QWs, tend to act as two (doubly) degenerate states. Similarly, the total energy for each eigenstate was found to start converging to a constant value for spacer thicknesses of 30 nm and beyond. This implies that for a spacer thickness of 30 nm and above, the QWs are essentially uncoupled and the effective band gap (e (n=1) to hh (n=1)) settles at ~0.743 meV. This behavior could be influenced by other factors, such as the width of the QWs and the effective masses of the carriers.

Chapter 9

Growth of stacked layers of InSb/GaSb quantum dot structures

Vertical stacking of QD layers have been reported to induce the nucleation of the individual QDs on top of each other, a characteristic attributed to the strain effect of the underlying QD, provided that the spacer thickness is not too large [17]. Various studies have been performed to examine the influence of stacking on low dimensional systems, such as QDs. Experimental results and theoretical predictions [107]have confirmed that the geometry of dots and their distribution can be enhanced by stacking. This could be achieved through the growth of successive dot layers of specific thickness (separated by a spacer), which invariably stimulates the fabrication of dots with uniform size and spacing, considering the fact that the overlying islands are prone to mirror the buried islands and simultaneously nucleate directly above it. Multilayers of QDs have also been reported [108] to be crucial for effective infrared absorption; however, stacking can also result in the formation of defects due to strain relaxation, while the stacking array of atomic layers during growth influences the periodicity of the atomic arrangement in the material [109].

Despite significant efforts dedicated to the fabrication and study of stacked QD multilayers, very little literature is available on the effect of stacking on the PL properties of QD structures. This section, therefore, aims at investigating how stacking influences the structural and PL properties of InSb/GaSb dot structures. In order to accomplish this objective, the growth and characterization of four different samples (denoted as samples A, B, C and D) which were grown consecutively using similar growth conditions, will be examined in this chapter. The samples were grown on GaSb ((100) 2° off towards <111>B \pm 0.1°) substrate using TMIn, TEGa and TMSb as source precursors. A more detailed description of the sample preparation and growth procedure has been presented in section 4.2 and 4.3 respectively.



Figure 9. 1. Cross-sectional representation of intended samples.

Figure 9.1 shows a schematic cross-section of the intended structures. The first three samples contained a 300 nm GaSb buffer layer and a 200 nm thick GaSb cap layer, with different numbers of InSb QD layers embedded between the GaSb buffer and cap layers for each sample. The fourth sample in which uncapped InSb dots were grown directly on a 300 nm GaSb buffer layer was used as a reference for SPM. Sample A nominally contained a single InSb QD layer, while samples B and C contained a stack of two and three InSb QD-layers, respectively. Each InSb layer in sample B and C was separated by a 30 nm-thick GaSb spacer layer. For samples A, B and C, an additional layer of uncapped InSb dots was deposited on top of the final GaSb layer under the same conditions as the embedded InSb dot layers for SPM studies. All four samples were deposited using identical growth conditions. The GaSb cap and spacer layers were grown at a temperature of 500°C at a nominal growth rate of ~2.7 Å/s. Prior to the growth of the dots, the 300 nm thick GaSb buffer layer was grown at a temperature of 550°C and a

growth rate of \sim 1.7 Å/s. The V/III ratio was fixed at 2.0 for the growth of the buffer layer, and was subsequently increased to 7.0 during the deposition of the spacer and cap layers respectively, while the InSb dots were deposited using a V/III ratio of 1.0.

9.1 SPM investigation and analysis of uncapped dots

Parameters such as the dot densities, heights and diameters, were deduced from SPM measurements on the uncapped dots in each sample, using the Bruker NanoScope analysis software (version 1.40). The sample containing no embedded dots (sample D) had a dot density $>10^{10}$ cm⁻², with lateral dimensions between 30 nm and 80 nm, and heights between 4 nm and 12 nm. However, a significant reduction in dot density (~ 8 × 10^9 cm⁻²) was noticed for the other three samples (samples A to C, which nominally contained embedded dots). Also the lateral dimensions increased to between 40 nm and 100 nm. The reduction in uncapped dot density for samples A to C (shown in the SPM image in Figure 9.2) is inferred to result from the condensation of Sb on the GaSb capping layer surface at low (non-ideal) temperatures [110]. This can enhance Sb segregation, and alter the geometry of the dots.



Figure 9. 2. SPM images showing the morphology and density (a) of uncapped dots for sample D grown directly on a GaSb buffer, and (b) of uncapped dots terminating the cap layer of sample C.

A comparison of the SPM images displayed in Figure 9.2 reveals a significant difference in the shape of dots grown directly on the buffer (see Fig. 9.2(a)) compared to those that terminating an "embedded-dot" sample (Figure 9.2(b)). The former have a pyramidal form with steep side facets, while the latter appear to have a truncated cone shape. The existence of strain at the surface of the samples due to the buried islands and the annealing step of the embedded dots during the deposition of the spacer and cap layers can alter the surface morphology of the cap and hence modify the dot morphology. Other factors which can modify the final surface of the cap layer and consequently the uncapped dot geometry include the difference between the buffer and cap layer thicknesses, and the variation in their respective growth temperatures from 550°C to 500°C during deposition.

9.2 STEM/TEM analysis of capped structures

The structural features of the capped samples were analysed in bright field (BF) and dark field (DF) imaging conditions, using both scanning transmission electron microscopy (STEM) and TEM, while information on the elemental composition of the samples was deduced using EDS. The cross-sectional TEM/STEM micrographs obtained for samples A to C, shown in Figure 9.3, reveal the transformation of the intended InSb QDs into QWs after capping. The dissolution of QDs have been reported [111] to occur progressively during the capping process. The presence of the capping layer is expected to induce strain in the buried dots besides protecting the QDs from exposure to ambient conditions, and is also fundamental in tailoring the band gap of the material. In order to detect luminescence, it was necessary to cap the dots. Factors such as the capping layer material, capping temperature and growth procedure are known to be vital to retain the dots after the deposition of the cap layer. In this study, a high growth rate $\sim >3.5$ Å/s (which in principle will reduce the time of annealing of the embedded dots and assist in retaining the original morphology) was found to be unfavourable for the deposition of a cap or spacer layer - it led to the propagation of growth defects such as threading dislocations. However, the prolonged annealing of the dots during the growth of the cap or spacer layer(s) at a low growth rate clearly induced intermixing/alloying which destroyed the buried QDs.



Figure 9. 3. (a) BF cross-sectional TEM micrograph of sample A, with the green line representing the position where an EDS line scan was performed. (b) DF cross-sectional TEM micrograph of sample B. (c) BF cross-sectional STEM micrograph of sample C, with the red circles (**0**₁ and **0**₃) indicating the spots where EDS point analysis was performed, and (d) BF cross-sectional TEM micrograph of sample C showing stacking faults.

According to the STEM and TEM micrographs in Figure 9.3(a-c), the presence of QWs at the interface between the GaSb cap, spacer and buffer layers suggests the occurrence of inter-diffusion of gallium (Ga) and indium (In) in the region(s) where the buried InSb dots were intended to be. The uncapped InSb islands terminating the samples appear to be unaffected, as seen in Figure 9.3(c) and (d). Some growth-induced defects were observed in sample C at the interface where the dots were expected to be, as shown in Figure 9.3 (d). These defects appear to be introduced as a result of precipitation/

formation of Sb crystallites or Ga/In droplets during growth process, which perhaps enhanced the aggregation of islands around this region, thereby promoting defect nucleation and incorporation. According to a previous study [112], the mutual nucleation of two islands can stimulate the interaction of defects in neighbouring islands, thereby forming extended defects at the boundary.



Figure 9. 4. A magnified image of Figure 9.3(d) clearly showing the stacking faults terminating at an uncapped dot on the surface of sample C.

Other features noticed in sample C in Figure 9.3(d) include a pair of stacking faults generated due to the disruption of the crystallographic planes during growth. The stacking faults appear to originate from the substrate and then extend through the buffer, spacer and cap layers towards an uncapped InSb island (width ~50 nm) on the surface. This is shown more clearly in Figure 9.4. The bright white line that runs along the surface of the capping layer as seen in Figure 9.4 originates from the mask (usually platinum) which was deposited over the area of interest and serves as a protective layer for the sample against damages such as scratches during ion milling.



Figure 9. 5. EDS line-scan taken from sample A, across the interface between the GaSb cap and buffer layers.

The EDS line-scan shown in Figure 9.5 was obtained from sample A at the position shown in Figure 9.3(a). The line-scan confirms the presence of In, Sb and Ga at the interface where the dots were expected. Many experimental studies and theoretical reports [113, 114, 115, 116, 117] (mostly for InAs/GaAs QD structures) have confirmed that substantial Ga and In inter-diffusion between the wetting layer (WL) and the 3D islands can alter the chemical composition of both of these from that of the actual deposited material [118].



Figure 9.6. DF cross-sectional STEM micrograph showing the interface (and spot of point analysis) between the buffer and cap layers where the dots are embedded in sample C.

The STEM micrograph of sample C displayed in Figure 9.6 was taken under high angle annular DF imaging conditions in scanning mode. Significant white contrast is seen in Figure 9.6. An EDS point analysis carried out in this region (analysis spot indicated by the red symbol **O**₂) confirmed the presence of indium in this region. Similarly, the presence of Ga and Sb within the interface region was also established as shown in Figure 9.7 (labelled spot 2), bearing in mind that only InSb was deposited at the interface region.

Galluppi *et al.* [119] were the first to detect In/Ga intermixing in nominally pure InAs dots on GaAs, and noted that the PL spectra from atomic layer MBE grown InAs QDs coincided energetically with those of In_{0.5}Ga_{0.5}As QDs grown using MOVPE. Their results indicated that Ga and In inter-diffusion, in addition to indium segregation, may play a role in QD self-assembly. Acapito *et al.* [118] confirmed this result by using extended X-ray absorption fine structure measurements to determine the composition and the state of strain in In_xGa_(1-x)As/GaAs QDs using a first shell bond length analysis. The measurements revealed an alloyed strained WL with \approx 15% indium concentration while the QDs comprised of a relaxed In_xGa_(1-x)As alloy with an indium content *x* \approx 40%. Similarly, by means of TEM and compositional profiling, the intermixing of Ga/In in InAs/GaAs self-assembled QDs has been reported [120] to cause a reduction in the maximum indium content in the WL from the actual amount deposited. Factors such as lower growth temperature was described to give rise to slightly weaker intermixing [120], while the

surface migration/diffusion of In atoms on the surface of the QD has also been reported [121] to influence intermixing and the dissolution of the QD apex.



Figure 9. 7. EDS spot analysis of cap layer region (depicted as spot 1), the interface between the buffer and cap layers where the dots are embedded in sample C (depicted as spot 2), and the uncapped dots terminating the cap layer of sample C (depicted as spot 3).

The results of the EDS spot scans displayed in Figure 9.7 were taken from sample C, with the analysis spots represented by the red symbols O_1, O_2 and O_3 in Figure 9.3(c) and 9.6. Results of the EDS scan on the cap layer (labelled spot 1 in Fig. 9.7) confirmed that the content of the cap layer is Ga and Sb, with no trace of In. However, the detection of both Ga and In within the interface region where the embedded dots were intended is an indication inter-diffusion. Penev *et al.* [122] studied the strain dependence of diffusion and has shown that In adatom diffusivity on the GaAs (001)-c(4×4) surface can be influenced considerably by the presence of strain. Likewise, results from the experimental confirmation of indium migration processes during the fabrication of InAs/GaAs quantum posts [123], has proved that the detachment and surface migration

of In adatoms due to non-uniform distribution of strain can lead to a transient reduction of stress during the deposition of indium.

EDS spot analysis was carried out on an uncapped island terminating sample C at the spot indicated by the red symbol O_3 in Figure 9.3(c), to determine whether or not Ga was present. The results are labelled spot 3 in Figure 9.7. No evidence of Ga was detected, unlike in the capped islands where significant amounts of Ga were observed. The uncapped islands thus only contain In and Sb. This supports the suggestion that the capping layer very often causes inter-diffusion, which accounts for the presence of Ga in the intended WL/QD layer, as shown in Figures 9.5 and 9.7.

9.3 An investigation of structural defects in the samples

An increase in the number of embedded layers of InSb dots from a stack of 2 layers to 3 layers stimulated the onset of various kinds of defects. Apart from the threading dislocation observed in sample 2, which contained a stack of 2 layers of InSb dots (see Figure 8.7), deviations of the stacking sequence of the atomic planes from the ideal sequence, and surface irregularities resulting from the nucleation of defects, were observed in the cross-sectional TEM micrograph of sample C, which nominally contained a stack of 3 layers of buried InSb dots, as shown in Figure 9.8.



Figure 9.8. BF cross-sectional TEM micrograph of sample C showing strain contrasts and stacking faults in the vicinity where QDs are expected.

The imperfections visible in Figure 9.8 are line and planar defects. Most of these defects were observed to extend from the GaSb substrate into the buffer layer and into the regions where the dots were expected to be situated. Similarly, a "v-shaped" defect consisting of twin pairs of either detached dislocations or stacking faults, which propagate in opposite directions, was observed in the BF cross-sectional TEM micrograph, shown in Figure 9.9.



Figure 9. 9. BF cross-sectional TEM micrograph showing a v-shaped defect.

This defect is identical to that reported for stacked, self-assembled InAs QDs grown by MBE on a GaAs substrate [124] [125] [126] and for a single layer of self-assembled InAs QDs grown on (100) semi-insulating GaAs substrate using low pressure (100 mbar) MOVPE [127]. The nucleation of a v-shaped defect has been reported [128] to occur on relief perturbations and along irregularities on the surface and can therefore be stimulated by non-optimal growth conditions.

The presence of surface corrugation was noticed in the DF cross-sectional TEM micrograph of sample C, as shown in Figure 9.10. The layer thickness fluctuations seems to be evident along the GaSb spacer layer interfaces close to the assumed position of the embedded dots and was observed in sample C while using two beam imaging.



Figure 9. 10. DF cross-sectional TEM micrograph of sample C showing surface corrugations.

Furthermore, the non-uniform thickness which is characterized by the presence of surface corrugation on the spacer and buffer layers can be induced by kinetic epitaxial growth instabilities resulting from non-ideal growth conditions. Also during the very destructive TEM specimen preparation procedure, the strained material is thinned down as much as possible (\sim 10 nm) to enable the transmission of electrons through the material. Thinning often generates thin-foil relaxation, which can cause distortion and non-uniformities in layer thickness.

9.4 PL characterisation of capped samples

Figure 9.11 shows the normalised low temperature (10 K) PL spectra obtained from samples A to C, as well as that of the GaSb substrate used. Sample D, which contained the uncapped dots gave no PL emission, a behaviour which is ascribed to non-radiative recombination at the surface. All the spectra in Figure 9.11 were collected using an excitation power of 105 mW. Three distinct low energy lines (absent in the substrate material) at ~748 meV, 740 meV and 733 meV can be associated with the epitaxial material in the grown samples, while the other two PL lines (denoted by A and BE₄ [93] [94]) have their origin in the substrate. The positions of the low energy lines, believed to

originate from unintentionally formed InGaSb/GaSb QWs vary for the three samples. Sample C, which contains three QWs, has the strongest low energy emission.



Figure 9. 11. Normalized low temperature PL spectra of samples A to C. A typical PL spectrum of the GaSb substrate is included for comparison.

The full width at half maximum (FWHM) of the emission lines were measured to be ~18 meV, 20 meV and 25 meV for samples A, B and C, respectively. Also, the emission wavelength red shifted as the number of layers increases, despite the layers having been deposited under similar growth conditions. A similar red shift of the PL emission line was observed [129] from the PL spectrum of three sheets of vertically coupled InSb QDs, separated by 5 ML GaSb spacers; stacking of the QDs was reported to induce a long wavelength shift of the QD PL lines, due to coupling between the dot layers. A 92 meV red shift in the PL emission line was first reported for multilayer, vertically coupled InAs/GaAs QDs grown by MBE [130]. The red shift was accompanied by a 25% reduction in PL linewidth, as the number of InAs islands (~4 nm high) separated by a GaAs spacer layer (~5.6 nm thickness) was increased from a single layer to a stack of 10 layers, and was attributed to vertical coupling of islands arranged in columns [130].



Figure 9. 12. (a) Normalised 10 K laser power dependent PL spectra of sample C. (b) Temperature dependent PL spectra (semi-log plot) of the low energy line in sample C

The behaviour of the PL spectra of Samples A and B with temperature and laser power was similar to that described for samples 1 and 2 in sections 7.3 and 8.2 respectively, and as such it will not be presented in this section. However, Figure 9.12(a) displays the normalised power-dependent spectra for sample C, showing ~3 meV blue shift as the excitation power increases. No significant broadening of the low energy line was observed. This behaviour confirms that the presence of a GaSb spacer, which was suggested in sub-section 8.2.1 to improve the quality of InSb layer deposited, is most likely responsible for the observed reduction in blue shift and line broadening of the low energy peak compared to samples without a spacer layer.

Figure 9.12(b) shows the temperature-dependent PL spectra obtained for sample C. It is clear that the low energy PL line quenches with temperature and its luminescence disappears completely at 90 K. A rapid quenching of the luminescence was observed for temperatures between 10 – 30 K, after which the rate of luminescence quenching was slower. Also, a lower value of apparent thermal activation energy, $E_a = 10.8 \pm 0.5$ meV, was determined for sample C. This is comparable to the thermal activation energy obtained for sample 2 in sub-section 8.2.1 ($E_a = 11.7 \pm 1.0$ meV) and displayed in Figure 8.5(b).

In conclusion, it can be inferred that the NIR low energy emission in the present work results from recombination in QWs rather than in QDs. The uncapped dots were transformed due to alloying, resulting from inter-diffusion of Ga and In at the interface where the embedded dots were intended. The extent of inter-diffusion is most likely to be enhanced due by indium adatom migration and prolonged effective annealing times after the deposition of the QDs. This may give rise to an inhomogeneous strain distribution, less uniform layers in terms of width and compositions that differ substantially from that of the InSb intended. This can account for the spectral shift in PL peak position and changes in emission linewidth. Results from this study indicate that inter-diffusion can be promising as a method for controlling the optical properties of QWs and tailoring the spectral response to desired emission wavelengths.

Chapter 10

Summary of results and conclusions

The growth of InSb quantum dots on GaSb ((100) \pm 0.1°, (111) \pm 0.1°, and (100) 2° off towards <111>B \pm 0.1°) substrates using atmospheric pressure horizontal MOVPE reactor has been investigated. This study was prompted by the uncertainties surrounding the emission wavelength and effective band gap of InSb/GaSb QDs, a topic on which no consensus has been reached to date. For instance, some reports have shown that the band alignment of InSb/GaSb QDs is weakly type-I in nature [34], while another study reported that these QDs have a type-II band alignment [10]. Similarly, different PL peak energies have been reported for these structures, with some groups reporting emission in the near-infrared region [6] [7] [8] and others reporting emission in the mid-infrared region (0.3 – 0.5 eV) [9].

QDs were deposited using MOVPE under different growth conditions (temperature and time) in order to vary the size, density and aspect ratio of the dots. All uncapped structures were analysed using both SEM and SPM, while all capped structures were analysed using PL spectroscopy and TEM (employing both bright field and dark field imaging conditions). The samples were also modelled theoretically using nextnanomat software to gain more insight into their behaviour, electronic structure and properties. The growth of InSb QDs on 2° off (100) GaSb substrate using a TDMASb precursor as the antimony source revealed the sensitivity of the surface morphology to growth temperature and V/III ratio, with the best surface morphology obtained using a V/III ratio of 1.0 and a growth temperature of 425°C, an observation which seems to be in agreement with previous studies [78].

Similarly, the simultaneous growth of InSb dots on two different GaSb substrate orientations (2° off (100) and (111)) using TMSb as the antimony source revealed a lower growth rate for the dots grown on the (111) substrate. The lower growth rate was confirmed by the slight reduction in dot density measured for the dots grown on a (111) substrate as the V/III ratio was increased. The reduction in dot density as the V/III ratio increased is attributed to the reduced number of indium adatoms on the growth surface.

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This stimulates a decrease in the migration length of indium species due to the increased probability of encountering Sb-adatoms. Likewise, the SPM size distribution analysis of the samples revealed a higher dot density for uncapped samples grown on (100) GaSb substrate. The misorientation of the (100) substrate was suggested to enhance the formation of surface steps, which provides low energy growth sites, and hence promotes island nucleation. Also the presence of the atomic steps on the (100) substrate reduces the mobility of the surface absorbed species thereby enhancing the sticking coefficient of adatoms on the (100) surface compared to the (111) surface.

Investigations of the influence of the buffer layer thickness on the formation of uncapped dots showed that buffer layer thicknesses less than 250 nm resulted in surface corrugations (multi-step formation). Dots grown on GaSb buffer layers having thicknesses between 150 nm and 250 nm were found to possess a truncated cone shape with a flat vertex , while those grown on a much thinner buffer layer (50 – 100 nm thick) were almost dome shaped. The corrugated buffer surface was observed to enhance the degree of order in the arrangement of the dots, with surface troughs appearing to act as favourable nucleation sites for 3D islands.

10.1 TEM characterisation

The epitaxial growth of InSb/GaSb is expected to start off 2-dimensionally, with the formation of a thin wetting layer, which serves as a platform for the nucleation of 3D defect-free nanometer-sized islands. The islands usually emerge when a critical thickness is exceeded. The wetting layer is understood to consist of a thin layer of a narrower bandgap semiconductor embedded between thicker materials with a wider band-gap (typically between a few unit cells thick). It is most often conceived as an ultra-narrow rectangular-like QW (from an electronic structure point of view [120]). However, the TEM micrographs obtained from the capped samples in this study revealed only QW-like structures rather than contrast arising from QDs. The QWs were observed at the interface between the buffer and capping layers. Quantified EDS line scans across the interfaces where the dots were expected indeed confirmed the presence of a both In and Ga in the regions where pure InSb was expected, with an indium content of approximately 17%. Bearing in mind that QDs were distinctly visible in the uncapped samples, it was suggested that the disappearance of the dots in the capped samples resulted from inter-

diffusion between gallium and indium at the interface between the GaSb buffer and cap layers, which most likely occurred during the capping of the InSb QDs.

10.2 Photoluminescence characterisation

Low energy PL emission ascribed to the epitaxial "InSb" were observed in all capped samples at near-IR wavelengths (1650 – 1720 nm). This emission corresponds to the PL energies (0.72 – 0.75 eV) previously reported [6] [7] [8], but which were ascribed to emission from InSb QDs. The low energy PL from the epitaxial "InSb" were unstable at higher temperatures and typically disappeared at sample temperatures ~80 K. Similarly, these lines exhibited a blue shift as the excitation power increased.

Uncapped QDs yielded no PL due to surface recombination. Systematic changes in the mole fraction of TMIn and TMSb during deposition of the capped samples were observed to prompt a shift in the PL emission lines, an attribute ascribed toan interplay between different size distributions before capping and quantum confinement in the QWs that unintentionally formed during capping. Also, an increase in the number of InSb layers separated by GaSb spacer layers was observed to induce a red shift in the low energy lines and a strengthening of the PL emission.

No PL emission was detected in the mid-IR region in any of the samples characterised via PL spectroscopy. To date, Tasco *et al.* [9] are the only authors to have reported emission in the mid-IR region for InSb/GaSb QDs. It is important to note that the InSb/GaSb QD structures studied by Tasco *et al.* [9] were grown by MBE, and slightly different from the QD structures grown in this study, since the GaSb buffer and cap layers containing the buried InSb dots were both confined on each side (before the buffer layer and after the capping layer) by 100 nm thick p-type and n-type AlGa(As)Sb claddings [33]. The presence of the Al-containing layer can improve trapping by the dots and hence gives rise to better confinement and enhanced optical luminescence. However, the structures grown in this investigation do not contain any cladding layers, apart from the GaSb cap layer. According to the TEM analysis in the present study, the existence and/or formation of QWs rather than QDs was clearly evident for all the capped samples studied. The presence of extended defects and dislocations in the vicinity of the QWs (especially for sample C), made it challenging to precisely deduce the exact nature of the observed dot-like features. With this information, this study suggests that the low energy PL lines

observed in the near-IR region in the capped samples are due to transitions within InGaSb/GaSb QWs, while the shift and broadening of the PL peak with increase in excitation power could be as a result of local differences in the nominal thickness of the QWs [131] [132], as well as local variations in alloy composition.

10.3 Conclusions

In conclusion, this study suggests that it is possible to inadvertently form InGaSb QWs rather than InSb QDs during the fabrication of InSb/GaSb QDs. The annihilation of the QDs is presumed to occur during the capping process and deposition of the spacer(s), giving rise to QWs. However, it was previously reported that the actual composition of InSb QDs embedded in a GaSb matrix will not be pure that of InSb, but rather InGaSb, a phenomenon attributed to the intermixing of Ga/In driven by thermodynamics [133]. This seems to be in good agreement with the results obtained in this study. The inclusion of a GaSb spacer layer was found to reduce the blue shift and broadening of the PL emission line as the laser power was increased. This occurred as a result of improvements in the quality and uniformity of the subsequent InSb layer. A change in the growth rate of the samples was observed to simultaneously induce a shift or systematic modification in the PL emission energy of the deposited material system, an occurrence which is representative of the quantum confinement effect. An increase in the number of "InSb" dot layers was observed to induce a long wavelength shift of the low energy PL lines from the unintentional QWs that formed, and an increase in the FWHM and intensity of the PL. The long wavelength shift and changes in spectral linewidth of the NIR emission from the epitaxial InGaSb QWs was suggested to be stimulated by variations in layer thicknesses and alloy composition resulting from inter-diffusion of Ga and In during the prolonged effective annealing time of the QDs (during spacer/cap layer deposition).

10.4 Challenges

A few challenges were encountered during the course of fabricating the proposed InSb/GaSb QD structures. As a result of the low melting point of InSb (~527°C), one of the major challenges confronted was the difficulty in obtaining an optimised GaSb capping layer grown at relatively lower temperatures using TMSb as precursor. As mentioned, TMSb pyrolysis at relatively high temperatures in a H₂ ambient. TDMASb, which in principle is more suitable in this regard, tended to enhance the incorporation of

nitrogen impurities at temperatures above 400°C and thus produced samples with poor surface morphology and weak PL emission. The best PL emission was obtained from samples which were capped at relatively low growth rates, using higher V/III ratios (between 2.0 and 7.0). Also the "ideal" growth conditions which were finally adopted for the deposition of the cap layer in this study was such that ample time was allowed for the growth of a fairly thick cap layer. This makes the buried dots vulnerable to post-thermal annealing and increases the chances of intermixing.

10.5 Proposed future work

Further investigations will be carried out by confining the InSb QDs (buried between two GaSb barrier layers) on both sides using thick AlGa(As)Sb, lattice-matched cladding layers similar to those reported by Tasco *et al.* [9], so as to enhance carrier confinement and improve the luminescence from the samples. In addition, the subsequent growth of InSb QDs will be carried out on a different substrate (such as InAs) for comparison.

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