Layer Perfection in Ultrathin InAs Quantum Wells in GaAs(001)

by

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Abstract

Single- and sub-monolayer (ML) InAs films buried in GaAs(001) were grown by metalorganic vapor phase epitaxy (MOVPE) and atomic layer epitaxy (ALE). X-Ray standing wave (XSW), high-resolution X-Ray diffraction (HRXRD), and photoluminescence (PL) measurements were used to assess the layer perfection and positions of 1 and 1/2 ML InAs quantum wells within the GaAs matrix. Local structure in the 1 ML films was evaluated using glancing-incidence X-Ray absorption fine structure (XAFS) measurements performed at the In K-edge.

Growth temperature effects were studied in a series of samples produced between 400 and 600°C. The XSW coherent position of the In atoms decreased with increasing temperature in the 1 ML samples, suggesting an optimal growth temperature near 550°C, according to the agreement between the data and the macroscopic elastic theory prediction of a 15% displacement of the In atoms from the GaAs(004) planes, along the growth direction. The XSW coherent fraction indicates that approximately 80% of the In atoms in this sample reside in the ideal position, a more uniform In distribution than previously reported. Low temperature PL measurements reveal that the sharpest In-excitonic emission is obtained from the 1 ML sample grown at 530°C, further clarifying the conditions for producing the best films.

With decreasing growth temperature the XSW results may indicate segregation of In atoms into multiple layers. This effect is reduced at higher temperatures due to the favourable kinetic conditions created in the MOVPE environment. The most important factors are the high GaAs cap growth rate and the high As overpressure. Neither of these requirements is met by the ALE growth technique.

In-As bond lengths determined from the XAFS data also agree with the macroscopic elastic description; the In-As bonds undergo a very small ($\sim 1.8\%$) compression relative to their bulk bond lengths. Issues of InAs islanding were not resolved using this technique due to the low contribution of the second shell (In-In) to the XAFS signal and the very small magnitude of the bond-length distortions.

Issues of strain and bond-length distortions were further explored using $\text{In}_x\text{Ga}_{1-x}\text{As}$ thin-alloy films grown coherently on $\text{InP}(001)$. The In-As and Ga-As bond lengths in films of varying composition, x , were determined using Ga- and As-K edge XAFS measurements. Comparison with a random-cluster calculation demonstrates that the external in-plane epitaxial strain imposed by pseudomorphic growth opposes the natural bond-length distortions due to alloying.

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and encouraging in my efforts, through joyous and difficult times.

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Sarah has walked along beside me and been the sun in my Vancouver sky. Clichés aside, she has been my soulmate throughout.

Dedication

Press on. Nothing in the world can take the place of persistence.

Talent will not; nothing is more common than unsuccessful people with talent.

Genius will not; unrewarded genius is almost a proverb.

Education alone will not; the world is full of educated derelicts.

Persistence and determination alone are omnipotent.

I remember, Pop.

To my Parents.

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List of Abbreviations

- ADC - Analog-to-digital converter.
- AES - Auger electron spectroscopy.
- AFM - Atomic force microscopy.
- ALE - Atomic layer epitaxy.
- ALMBE - Atomic layer molecular beam epitaxy.
- BC - Boundary condition.
- BNL - Brookhaven National Laboratory.
- CB - Conduction band.
- CBE - Chemical beam epitaxy.
- CTR - Crystal truncation rod.
- CW - Continuous wave.
- DAFS - Diffraction anomalous fine structure.
- DAP - Donor-acceptor pair.
- DTXRD - Dynamical theory of X-Ray diffraction.
- EELS - Electron energy loss spectroscopy.
- EDR - Enhanced dynamic range.
- EDX - Energy-dispersive X-Ray spectroscopy.
- ETB - Empirical tight-binding.
- EXAFS - Extended X-Ray absorption fine structure.
- FFFS - Fourier-filtered first shell.
- FFT - Fast Fourier transform.
- FLY - Fluorescence yield.
- FME - Flow-rate modulation epitaxy.

- FT - Fourier transform.
- FWHM - Full-width at half-maximum.
- GID - Grazing incidence diffraction.
- GIXAS - Grazing incidence X-Ray absorption spectroscopy.
- GIXS - Grazing incidence X-Ray scattering.
- HREM - High-resolution electron microscopy.
- HRXRD - High-resolution X-Ray diffraction.
- HVPS - High-voltage power supply.
- LDA - Local density approximation.
- LM - Lattice-matched.
- MC - Monochromator.
- MCA - Multichannel analyzer.
- MEE - Migration-enhanced epitaxy.
- MET - Macroscopic elastic theory.
- MFC - Mass flow controller.
- ML - Monolayer.
- MOCVD - Metalorganic chemical vapour deposition.
- MOVPE - Metalorganic vapour phase epitaxy.
- MQW - Multiple quantum well.
- MS - Multiple scattering.
- NIM - Nuclear instruments module.
- NIST - National Institute of Standards and Technology (United States).
- NSLS - National Synchrotron Light Source.
- NLLSQ - Nonlinear least-squares.
- PL - Photoluminescence.
- PLE - Photoluminescence excitation.
- PSPD - Position-sensitive photodetector.
- QW - Quantum well.
- RADS - Rocking curve analysis by dynamical simulation.
- RBS - Rutherford backscattering.
- RDS - Reflectance difference spectroscopy.

- RHEED - Reflection high-energy electron diffraction.
- SCA - Single channel analyzer.
- SI - Semi-insulating.
- SIMS - Secondary ion mass spectroscopy.
- SL - Superlattice.
- SS - Single scattering.
- SSRL - Stanford Synchrotron Radiation Laboratory.
- SQW - Single quantum well.
- TBAs - Tertiarybutylarsine.
- TBP - Tertiarybutylphosphine.
- TEGa - Triethylgallium.
- TEY - Total electron yield.
- TDOA - Thermally detected optical absorption.
- TMGa - Trimethylgallium.
- TMIIn - Trimethylindium.
- UHP - Ultrahigh purity.
- UHV - Ultrahigh vacuum.
- UPS - Ultraviolet photoelectron spectroscopy.
- VB - Valence band.
- VCA - Virtual crystal approximation.
- VFF - Valence force field.
- VGF - Vertical gradient freeze.
- XAFS - X-Ray absorption fine structure.
- XANES - X-Ray absorption near edge structure.
- XPS - X-Ray photoelectron spectroscopy.
- XRD - X-Ray diffraction.
- XSW - X-Ray standing wave.

Chapter 1

Introduction

The electronics industry is dominated by products based on elemental semiconductor (silicon) technology. For light-emitting devices, however, compound semiconductors reign. Here bandgap-engineered materials structures of extraordinary complexity are now routinely produced and are gaining share in a market which is set to exceed \$1 trillion U.S. by the end of the twentieth century. These developments have been achieved through advances in semiconductor growth techniques such as metalorganic vapour phase epitaxy (MOVPE) and molecular beam epitaxy (MBE). For III-V compound semiconductors a myriad of possible structures can be produced by depositing layers of well-defined thickness and composition upon a substrate crystal which provides a structural "template" for the growth.

A single quantum well (SQW) of InAs in GaAs(001) constitutes one of the most highly-strained III-V heterostructures. This thesis deals with structures produced at the ultimate limit: a single or half monolayer (ML) of In atoms replaces a layer of Ga atoms in a GaAs crystal (Figure 1.1). The large lattice mismatch ($\sim 7\%$) between the constituent materials makes these systems ideal for the study of fundamental materials issues [1]-[4]. With even fractional ML In depositions, sharp and intense photoluminescence (PL) emission has been observed [5]. Additionally, very recent theoretical [6] and experimental [7] studies have re-emphasized the technological promise of InAs SQWs for highly efficient excitonic lasing.

For these ultrathin InAs layers buried in GaAs there is considerable interest in

Figure 1.1: A single layer of In atoms embedded in a GaAs(001) crystal. The dotted lines indicate (004)-planes. The In, Ga and As atoms are indicated by black, white and shaded circles, respectively.

determining the effect of the In distribution on the optical properties. The challenges involved in this study are manifold. Epitaxy of δ -doping layers of this type requires extremely accurate control of the growth parameters. Researchers have observed In segregation during the topmost GaAs layer deposition using a variety of surface-analytical, optical and structural techniques [8, 9]. Suppression or elimination of this In/Ga exchange is a principal requirement for the successful fabrication of “perfect” δ -layers. Subsequently, powerful characterization techniques are required to assess the epitaxial structures. Buried interfaces present an experimental challenge since the structural morphology can not be determined using standard surface science techniques.

Recently many reports have examined ultrathin InAs SQWs in GaAs including optical and structural investigations [5, 10] and characterization of laser diodes [7, 11,

12]. With reduced dimensionality there is a huge increase in the density of states: from delocalized electron properties to increasingly atom-like behaviour. 0-d (quantum dot) confinement is widely believed to be capable of producing large improvements in laser diode performance; the lasing threshold can be greatly reduced by increasing the electron-hole overlap. PL studies have suggested that subML systems of InAs in GaAs form self-organized 0-d or 1-d structures during epitaxial growth [13]-[15], although these optical studies do not provide a detailed description of the In distribution parallel or perpendicular to the growth plane.

In this work InAs SQW structures of 1 and 1/2 ML thickness were produced by MOVPE and atomic layer epitaxy (ALE). In conventional MOVPE, group III and group V metalorganic precursors enter the growth chamber simultaneously. Surface reactions at the heated substrate lead to dissociation of the metal atoms from the organic components, resulting in epitaxial growth. ALE is a variation of MOVPE in which the group III and group V precursors enter the chamber separately, with a hydrogen purge between each step. Layer-by-layer growth with ALE was supposed to produce sharp interfaces through self-limiting growth mechanisms [16].

For industrial applications, MOVPE and ALE, typically using pressures of ~ 50 Torr, have distinct advantages over MBE which requires ultrahigh vacuum (UHV). However, MOVPE is less mature than MBE in the *in-situ* monitoring of surface reactions because electron probe techniques, such as reflection high energy electron diffraction (RHEED), are prohibited at MOVPE pressures. In this work *in-situ* characterization was achieved using reflectance difference spectroscopy (RDS), which is sensitive to the presence and orientation of atomic surface reconstructions. For both MOVPE and ALE, detailed data describing the surface evolution during SQW growth sequences were obtained. For the MOVPE films, a novel technique exploited the reproducibility of multiple quantum well (MQW) growth cycles to obtain real-time spectroscopic data with extremely high temporal resolution.

High-resolution X-Ray diffraction (HRXRD) allows the determination of film thicknesses using the Pendellösung effect [10, 17]. This technique accurately determines the total dosage of InAs, but is rather insensitive to details of the In distribution. High-resolution electron microscopy has been used to study the cross-sectional properties

of MBE structures [18], but cannot resolve interfacial variations at the atomic scale. X-Ray absorption fine structure (XAFS) and X-Ray standing wave (XSW) measurements have been made on InAs MLs grown by MBE and have been successful in determining the perpendicular distance of In atoms relative to the GaAs (004) planes of the substrate (coherent position), the δ -like nature of the In distribution along the growth direction (coherent fraction), and the In-As bond lengths [2]-[4]. Another study considered the effect of segregation on the measured XSW parameters [1].

In this work, complementary short-range-order (XAFS) and long-range-order techniques (XRD, XSW) including element specificity (XAFS, XSW) were used to provide a detailed structural characterization and to furnish insight into the measured PL properties of these systems. Synchrotron X-Ray measurements were made at the Stanford Synchrotron Radiation Laboratory (SSRL) and the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The high photon flux provided by synchrotron radiation is essential for high-resolution studies of this type. Synchrotron X-rays are also preferred due to their intrinsic collimation, polarization, and their plane-wave-like properties. This work represents the first application of these techniques to MOVPE and ALE samples and the most comprehensive XSW and XAFS study of the effect of growth conditions on the In distribution.

This thesis is divided into eight chapters. Chapter 2 describes general aspects of the MOVPE and ALE techniques. Chapter 3 is devoted to dynamical diffraction in perfect crystals. The chapter begins with the development of the dynamical diffraction theory, and then considers the principles of XSW. Analysis of HRXRD data forms an integral part of the characterization process, and the theoretical background for these simulations is given in the last section of the chapter. Chapter 4 defines the XAFS and gives the mathematical expression used to analyze the experimental data. The electric field amplitudes of the waves travelling through layered structures during glancing-incidence reflection are considered using a recursive method. It is shown that this geometry also leads to an XSW field, which in this case extends far above the sample surface.

Chapter 5 summarizes the literature to provide a firm foundation in the theoretical and experimental precedents for this work. This includes discussions of strain,

structure and segregation in InAs SQWs in GaAs. RDS literature and optical studies of InAs SQWs are also briefly reviewed. In Chapter 6 a detailed description is given of the experimental apparatus used in the different components of this study, at SFU, SSRL and the NSLS. The experimental data are presented in Chapter 7 which is divided into sections devoted to analysis and interpretation of studies on several groups of samples. Specifics of the sample preparation appear in each section. A more general study of strained bond lengths in $\text{In}_x\text{Ga}_{1-x}\text{As}$ films grown on $\text{InP}(001)$ is also reported. Finally, important conclusions drawn from this work are summarized in Chapter 8, together with suggestions for future directions to be taken in this area of research.

Chapter 2

Metalorganic Vapour Phase Epitaxy

For epitaxial growth of thin-film semiconductors two dominant techniques have emerged, MOVPE and MBE. The former was originally called metalorganic chemical vapour deposition (MOCVD) by Manasevit who pioneered the technique in the late sixties [19]. International conferences have adopted the MOVPE acronym, which emphasizes the epitaxial nature of the process.

As the name suggests, MOVPE involves the transport of metalorganic precursor molecules to a heated single crystal substrate. At the vapour/solid interface complex chemical reactions occur with two principal results: the decomposition of the precursor molecules and the incorporation of metal atoms into the crystal. The latter process usually involves the arrangement of the metal atoms in registry with the single crystal matrix. For zincblende compound semiconductors, which are exclusively studied in this work, the group III and group V atoms provided by the precursors reside in their appropriate positions in the epitaxial film and continue the lattice structure of the substrate.

The MBE process is similar, but involves the use of elemental sources, with the process occurring in an ultrahigh vacuum ambient. In this respect, MBE is more challenging than MOVPE, which can produce very good results over a wide range of pressures from 1 atmosphere downwards.

For heteroepitaxy, the process is more complicated. The deposited thin film does not necessarily contain the same atomic species as the substrate, and may thus have a different native lattice constant from that of the substrate. Epitaxial films with larger lattice dimensions than the substrate would then experience a compressive biaxial strain in order to maintain registry with the substrate. Likewise, films with dimensions smaller than the substrate undergo tensile strain. This aspect of the heteroepitaxy must be carefully considered in the selection of appropriate materials for given device applications. Strain in MOVPE-grown films will form a major component of this thesis and will be discussed in some detail in Section 5.1.

In this chapter the MOVPE process will be described. Beginning with a summary of precursor containment and delivery to the reactor, details of the molecular decomposition at the crystal surface will be described. We can then discuss the incorporation of metal atoms into the crystal.

2.1 Source Precursors

Metalorganic source chemicals used in this work are contained in stainless steel “bubblers”, shown schematically in Figure 2.1. The carrier gas, in this case palladium-purified hydrogen, flows into the inlet of the bubbler, which is maintained at a constant pressure. The source chemicals are usually in liquid form although the indium source employed in this work, trimethylindium (TMIn), $(\text{CH}_3)_3\text{In}$, is solid at room temperature. In either case the H_2 gas delivers precursor molecules from the vapour phase towards the reactor, where the growth ultimately proceeds. In the SFU facility, both group III and group V elements are supplied by metalorganic sources of this type. Traditionally, the group V elements were supplied by hydride sources such as arsine (AsH_3). Among the advantages of the metalorganic group V sources (e.g. tertiarybutylarsine (TBAs), $(\text{C}_4\text{H}_9)\text{AsH}_2$; tertiarybutylphosphine (TBP), $(\text{C}_4\text{H}_9)\text{PH}_2$) are reduced toxicity, improved safety and lower decomposition temperatures. Two gallium sources were used in this work, triethylgallium (TEGa), $(\text{C}_2\text{H}_5)_3\text{Ga}$ and trimethylgallium (TMGa), $(\text{CH}_3)_3\text{Ga}$.

The partial pressure of the precursor vapour in the bubbler depends on the bubbler

Figure 2.1: Prepurified hydrogen gas flowing through a stainless steel bubbler containing liquid source metalorganic molecules. The saturated vapour is transported from the bubbler outlet downstream towards the reactor vessel. (From Arès [16]).

Precursor	a	b (K)	T_b (K)	P_b (Torr)	P_l (Torr)	f'_P ($\mu\text{mol}/\text{min}/\text{sccm}$)
TMGa	8.501	1824	263	1200	37.1	1.42
TEGa	9.172	2532	291	780	2.99	0.172
TMIn	10.52	3014	291	800	1.47	0.0823
TBAs	7.243	1509	280	800	71.9	4.41
TBP	7.586	1539	280	800	124	8.17

Table 2.1: Material parameters for precursors used in this work.

temperature according to

$$P_l(\text{Torr}) = 10^{[a-b/T_b]} \quad , \quad (2.1)$$

where the bubbler temperature, T_b , is measured in degrees Kelvin. Bubbler temperatures are maintained using temperature baths as shown in Figure 2.1. The constants a and b may be found from manufacturers' specifications for a given source.¹ Relevant data for sources used in this work appear in Table 2.1.

The flow rate of hydrogen into the bubbler is adjusted by mass flow controllers (MFCs) which allow a stable quantity of gas to flow per unit time. The molar flow

¹e.g. Epichem, Inc. product literature

rate, f_P , is then found from the relation

$$f_P = \frac{F}{C} \left(\frac{P_l}{P_b - P_l} \right) . \quad (2.2)$$

Here P_b is the bubbler pressure and $C = 22407.47$ is the volume in cc of 1 mole of an ideal gas at STP. F represents the volume flow rate in standard cubic centimetres per minute (sccm). Defining the quantity $f'_P \equiv f_P/F$, we find calculated values as shown in Table 2.1. Figure 2.2 illustrates the structure of two of the precursor molecules used in this work.

Figure 2.2: Precursor molecules: a) trimethylgallium b) tertiarybutylarsine. The large grey circles, smaller grey circles and empty circles represent metal atoms, C atoms and H atoms, respectively.

2.2 Reactor Flows

The saturated hydrogen gas transports the precursor molecules to the reactor through stainless steel tubing at ambient temperature. To prevent condensation of the precursor molecules inside these tubes, source chemicals must meet the requirement of a relatively high vapour pressure at temperatures at or below ambient. Moreover, reactions between group III and group V molecules prior to their arrival at the substrate

are to be avoided. To this end, the Thomas Swan MOVPE system employed in this work features separate lines for group III and group V gas transport to the reactor.

For stable molecular flows required to achieve reproducible results a number of factors must be considered. The bubbler temperatures and pressures must be accurately maintained, according to the discussion of the previous section. As well, the MFCs must supply a well-defined quantity of gas through the bubblers. This is achieved in part by operating the MFCs in a range from about 5 % to 100 % of their full scale supplies. This avoids the lower range where the flow might be most susceptible to small fluctuations. Additionally, the MFC flows are allowed to stabilize over a period of 5 to 20 minutes before initiating the precursor flow to the reactor. The Thomas Swan system employs a run-to-vent switching scheme which diverts the flow of a given species from the reactor, while allowing the flow to stabilize. The flow may then be rapidly directed towards the reactor at the appropriate time in the growth cycle. Details of the system are described in Section 6.1.

A very short distance from the reactor chamber, the metalorganic vapours are mixed together in a nozzle to promote uniformity. The mixture then travels towards the substrate. Within the reactor, complex hydrodynamic processes occur. Ideally, one wants a steady, laminar gas flow with few eddy currents or recirculating flows. In practice, this is difficult to achieve. Computer simulations have been developed to address this issue [20]. Alternatively, several guidelines exist for successful reactor design [21]. These involve avoiding the presence of sudden changes in reactor diameter, the presence of obstacles and recirculating convection currents due to the heating of the gases at the substrate. These factors can all limit the ability of reactors to produce uniform growth rates and abrupt changes in solid composition.

For the growth of InAs films in GaAs in this work, a vertical reactor geometry was employed. Although these reactors can produce outstanding results, it has been noted [21] that recirculating regions may be produced. These can enhance premature reactions and make rapid change of gas-phase composition impossible. A solution which is now commonly employed (but was not adopted in this work) involves spinning the susceptor rapidly to sweep the gas across the substrate. In this work a low pressure of 50 Torr was used to minimize the eddy currents in the cell. A schematic of the

vertical reactor cell appears in Figure 2.3.

Figure 2.3: The vertical reactor cell employed in this work. Gases travel downwards from the mixing nozzle towards the substrate which sits upon the heated susceptor. The susceptor temperature is measured by an infrared optical pyrometer which views the bottom of the susceptor. This temperature is regularly calibrated using a thermocouple placed directly on the top susceptor surface.(From Arès [16]).

Directly above the substrate a region exists where the gas flow is directed parallel to the sample surface. The transport of precursor molecules to the growing surface is achieved exclusively by the diffusion of the molecules through this “boundary layer” region. In the boundary layer there is no significant movement of the carrier gas perpendicular to the sample surface. This aspect of MOVPE is remarkably different from the MBE process which involves simple, ballistic transport of source molecules towards the substrate.

2.3 Precursor Decomposition

Within the boundary layer, complex chemical reactions result in the dissociation of the source molecules into new species, and provide the necessary metal atoms to the growing surface. The reactions may be classified as homogeneous or heterogeneous.

depending on whether molecules of different types interact separately, or with one another in the decomposition.

Pyrolysis of different precursor molecules is discussed at length in Reference [21]. Conflicting mechanisms are sometimes deduced and point to the difficulty in uncovering the details of processes occurring in the “messy” MOVPE environment. We consider the decomposition of the source compounds used in this work.

TMGa (see Figure 2.2) and TMIIn decompose by a simple homolytic fission reaction producing methyl radicals. The reaction is thought to proceed in three steps:

Methyl radicals produced in these reactions are removed from the surface by H atoms, which result from the decomposition of the group V precursors, as will be discussed. For TMIIn, the pyrolysis occurs at fairly low temperatures, with 100 % decomposition achieved as low as $\sim 350^\circ\text{C}$.

TEGa pyrolyzes homogeneously to produce diethylgallane and ethene molecules through the following so-called β -elimination reaction:

Complete decomposition by this mechanism occurs by about 350°C .

The decomposition mechanisms for the tertiarybutyl compounds are slightly more complex. An advantage of these sources is that decomposition occurs at lower temperatures than for the hydrides, allowing greater flexibility in determining suitable temperatures for a given process. Several possible reaction mechanisms exist:

There is compelling evidence [21] that tertiarybutylphosphine (TBP) decomposes according to the following mechanisms which seem to occur with no dependence on the group III source.

% Decomposition	AsH ₃	TBA _s	PH ₃	TBP
25	650	280	600	420
50	680	300	700	450
75	700	350	800	475
100	760	475	850	550

Table 2.2: Decomposition profiles of hydride and tertiarybutyl group V sources. Temperatures are given in °C. From Air Products and Chemicals, Inc. product literature.

The tertiarybutyl sources have temperature decomposition profiles as indicated in Table 2.2. From the table it is clear that the organic sources have advantageous properties when compared with the hydrides.

2.4 Incorporation into the Solid

From the boundary layer, the metal atoms must be adsorbed to the solid surface for epitaxy to proceed. There are in fact several phenomena occurring simultaneously: adsorption, desorption, surface diffusion, surface reactions, and attachment at kinks on step edges [21].

The epitaxy itself is driven by thermodynamics at the solid-vapour interface. Briefly, the supersaturation of the vapour drives the system from equilibrium between the solid and vapour phases. The system strives to reduce the difference in chemical potentials of the two phases,

$$\Delta\mu = \mu_v - \mu_s, \quad (2.3)$$

where μ_v and μ_s are the chemical potentials of the vapour and solid phases, respectively. The premise is elucidated succinctly by Stringfellow:

“A nonequilibrium situation is intentionally created that drives the system to produce the solid desired.”²

Several other factors are involved besides thermodynamics. Kinetics define the rates at which processes occur, while hydrodynamics and mass transport control the rate of material transport to the growing solid-vapour interface. It is often possible to determine the rate-limiting step in a given growth process by examining the temperature dependence of the growth rate, R_g , defined as the thickness of material deposited per unit time. An illustration of the various regimes is given in Figure 2.4.

Figure 2.4: Different regimes of epitaxy according to the growth temperature, T_g .

In conventional MOVPE, the growth is usually carried out in the mass-transport-limited region. Here the growth rate is independent of temperature, but depends linearly on the total flow. In ALE, the growth is necessarily surface-kinetic-limited. This technique will be discussed in more detail in Section 2.5.

In the mass-transport-limited regime, for many materials the growth rate is independent of the group V flow and depends only on the group III flow. In this situation essentially all of the group III atoms arriving at the growing surface are incorporated into the crystal from an excess group V vapour environment. This is not the case for

²Reference [21], p. 106

some alloy materials (e.g. GaAsSb) which require V/III ratios of very close to unity for successful growth [21].

In practice it is not possible to obtain perfectly flat, single-crystal substrates. Even the best available GaAs crystals contain a residual miscut. This means that the crystal surface is misoriented by some small angle with respect to the crystal planes. In this work (001)-oriented substrates were used exclusively, with typical miscut tolerances of $\pm 0.1^\circ$ from the exact orientations. With such small misorientations, the sample surface is usually characterized by large, uniform terraces of several hundred or thousand angstroms in width. For example, terraces of 1 ML height on a GaAs(001) surface with 0.1° misorientation would have widths of ~ 1621 Å. A fundamental mechanism of crystal growth thus involves the adsorption of metal atoms at the edges of atomic steps in the crystal. The step edges have a large number of available bonds and thus provide favourable sites for chemisorption. "Step flow" conditions, often encountered in MOVPE, refer to the process in which incoming species migrate along the crystal surface towards step edges where adsorption occurs. This results in the continuous growth of the atomic steps, and the propagation of the steps until either coalescence with another step, or an interruption at the edges of a sample. An illustration of the step flow growth mode appears in Figure 2.5.

The structure of the growing surface is actually rather complicated and can involve so-called reconstructions. It is energetically favourable for dangling bonds at the surface to rearrange themselves in their bonding configurations with their neighbours, often atoms of the same species. For instance, As atoms in a GaAs crystal always have four bonds to neighbouring Ga atoms within the bulk.³ On the surface, however, it is common for the As atoms to bond to one another. In the MOVPE GaAs growth sequences employed in this work, the group V molar flow rate is usually many times greater than the group III rate; the V/III ratio is usually quite high. Under these conditions it is common to find As-rich surfaces during growth, where the crystal surface may contain two or more layers of As atoms in some reconstruction. A more complete discussion of surface reconstructions during growth will appear in Section 5.3.

³An exception is the occupation of a Ga site by an As atom which creates an antisite defect, known as EL2, in the crystal [21].

Figure 2.5: A schematic illustration of step flow growth. The deposited adatoms incorporate only at steps.

2.5 Atomic Layer Epitaxy

A thorough discussion of ALE growth mechanisms has been given by Arès [16]. In this section a brief discussion of the technique will be presented in connection with the InAs SQW growth sequences described in Sections 7.3-7.5.

As mentioned, ALE is a variation of the MOVPE technique in which the cation and anion species flow to the crystal surface at separate times. A typical GaAs growth sequence involves a TMGa pulse of a few seconds duration, a H_2 purge, a TBAs pulse of a few seconds duration, and a second H_2 purge. The goal of this technique is to produce atomically flat interfaces as a result of the high cation mobilities in the absence of an accompanying anion flux. ALE growth is usually carried out in a “self-limiting” regime. Here the cation species are chemisorbed onto the crystal until the incorporation reaches a level of a single monolayer. No additional material is subsequently adsorbed.

For homoepitaxy, ALE has indeed been able to produce material of exceptional surface quality [22]. There are two main drawbacks to the technique. First, it seems that the chemical mechanisms which permit the self-limiting behaviour rely upon

methyl radicals bonded to the group III atoms in the top ML of the crystal [16]. While these radicals prevent the adsorption of more than 1 ML of material, they result in the incorporation of excess C atoms in the crystal. As a result, ALE-grown GaAs using TMGa is usually found to be p-type with carrier concentrations of approximately 10^{18} cm^{-3} . Conventional MOVPE growth of GaAs using TEGa usually results in n-type material, with carrier concentrations of 10^{15} cm^{-3} or less.

Secondly, the high cation mobilities can contribute to the segregation of one atomic species in heteroepitaxy of quantum wells, for instance. In the absence of a group V flux, the surface is more susceptible to group III atomic rearrangements near the surface. Although one can produce highly uniform and smooth quantum well layers, it is difficult to bury the layers at their nominal positions for use in quantum-well devices. In this work, In atoms deposited on GaAs surfaces are prone to exchanging positions with incoming Ga atoms during the GaAs cap layer growth, resulting in In atoms floating atop the growing GaAs layer. This segregation phenomenon presents a challenge for the production of δ -like single ML films of InAs in GaAs and will be discussed in detail in Section 5.2.

Having now described the underlying principles of the epitaxial growth methods used in this work, we are in a position to consider the analytical techniques which have been used to characterize the films. For layered structures, a standard laboratory technique is HRXRD which will be described in the next chapter. In this thesis different aspects of the dynamical diffraction are exploited, including the presence of a standing wavefield in perfect crystals during Bragg diffraction. The basis for these techniques will now be presented, followed by a discussion of glancing incidence XAFS. Finally, other *in-situ* and *ex-situ* techniques will be discussed.

Chapter 3

Dynamical X-Ray Diffraction

For diffraction of X-rays by perfect crystals, such as the epitaxial layers studied in this work, the underlying principles are described by the dynamical theory of X-ray diffraction (DTXRD) [23, 24]. In this chapter the development of the theory will be described in a manner which permits the application in the XSW technique, as well as in the HRXRD method. In the latter, a method of solution will be outlined which is attributed to Takagi [25] and Taupin [26] and is the basis for studies of layered structures.

3.1 Wavefields in Crystalline Media

For large perfect crystals the diffraction process must be described by considering the electromagnetic wavefield in the crystal as a single entity [23]. This distinguishes the dynamical approach from the simpler kinematical description which may be used for powder samples. In the diffraction process the incident and diffracted beams are coherently coupled, allowing energy to be exchanged between them. In the usual picture, diffraction occurs if the Ewald sphere of radius $1/\lambda$ passes through the origin of the reciprocal lattice and has its centre along the incident beam direction, while passing through a given reciprocal lattice point (Figure 3.1). Here λ is the X-ray wavelength. This geometry satisfies Bragg's law relating the diffraction angle, θ_B ,

and the spacing of the crystal diffraction planes, d_H ,

$$\lambda = 2d_H \sin \theta_B \quad . \quad (3.1)$$

Figure 3.1: The Ewald sphere and Bragg's law. The incident wave (I_0) with wavevector $\vec{K}_0$ is diffracted by the lattice planes with spacing d_H and reciprocal lattice vector $\vec{H}$ into the diffracted wave (I_H) with wavevector $\vec{K}_H$. The X-Ray wavelength, λ , is related to the wavevector as $\|\vec{K}_0\| = 1/\lambda$. The figure illustrates the situation in real and reciprocal space.

The basis for the dynamical theory, pointed out by von Laue [27], is the solution of Maxwell's equations in a medium with a periodic, anisotropic, complex dielectric constant. The electron density at a position $\vec{r}$ in the crystal may be expressed [23] as a Fourier sum over the reciprocal lattice as

$$\rho(\vec{r}) = \frac{1}{V} \sum_H F_H \exp(-2\pi i \vec{H} \cdot \vec{r}) \quad . \quad (3.2)$$

Here V denotes the volume of the unit cell and $\vec{H}$ is a reciprocal lattice vector with

Miller indices (hkl). The structure factor is then given by

$$F_H = \int_V \rho(\vec{r}) \exp(2\pi i \vec{H} \cdot \vec{r}) dV = \sum_n f_n \exp(2\pi i \vec{H} \cdot \vec{r}_n) , \quad (3.3)$$

where the sum is over all atoms in the unit cell, and f_n is the atomic scattering factor of atom n . Details of the calculation of F_H for a zincblende semiconductor are given in Appendix A. The electric displacement, $\vec{D}$, is defined as

$$\vec{D} = \epsilon \vec{E} = \kappa \epsilon_0 \vec{E} = \epsilon_0 \vec{E} + \vec{P} , \quad (3.4)$$

where ϵ is the permittivity of the material, $\vec{P}$ is the polarization, $\vec{E}$ is the electric field amplitude, and ϵ_0 is the permittivity of free space. The dielectric constant of the material is given by

$$\kappa = \epsilon / \epsilon_0 = 1 + \chi , \quad (3.5)$$

where χ is the electric susceptibility. In terms of the electron density, the dielectric constant may be written [23] as a function of position

$$\kappa(\vec{r}) = 1 - r_e \frac{\lambda^2}{\pi} \rho(\vec{r}) , \quad (3.6)$$

where $r_e = e^2 / 4\pi\epsilon_0 mc^2$ is the classical electron radius (2.82×10^{-5} Å). It is convenient to define $\Gamma \equiv r_e \lambda^2 / \pi V$, from which it follows that

$$\kappa(\vec{r}) = 1 - \Gamma \sum_H F_H \exp(-2\pi i \vec{H} \cdot \vec{r}) . \quad (3.7)$$

The atomic scattering factor is modified by the anomalous dispersion corrections which include effects of scattering and absorption, i.e. $f_n = f_n^0 + f_n' + i f_n''$. Hence, $F_H = F_H' + i F_H''$.

Neglecting the electric displacement current and assuming that the medium has a magnetic permeability equal to that of free space, $\mu = \mu_0$, Ampere's law becomes

$$\nabla \times \vec{\mathcal{H}} = \frac{\partial \vec{D}}{\partial t} = \epsilon_0 \frac{\partial \kappa \vec{E}}{\partial t} \approx \epsilon_0 \kappa \frac{\partial \vec{E}}{\partial t} , \quad (3.8)$$

while Faraday's law is

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} = -\mu_0 \frac{\partial \vec{\mathcal{H}}}{\partial t} . \quad (3.9)$$

The solutions for the field vectors, $\vec{E}$, $\vec{D}$, and the magnetic vector, $\vec{\mathcal{H}}$, are assumed to have the form of plane waves, i.e.

$$\vec{E}(\vec{r}) = [\sum_H \vec{E}_H \exp(-2\pi i \vec{H} \cdot \vec{r})] \exp(-2\pi i \vec{K}_0 \cdot \vec{r}) \exp(2\pi i \nu t) \quad , \quad (3.10)$$

and similarly for $\vec{D}$ and $\vec{\mathcal{H}}$, where ν is the frequency of the wave [23]. These solutions have the form of Bloch waves in the periodic material, and conservation of momentum has been included through Bragg's law, relating the incident and diffracted wavevectors through the relation

$$\vec{K}_H = \vec{K}_0 + \vec{H} \quad . \quad (3.11)$$

Substituting Equation 3.10 into Maxwell's equations, it is found that

$$\vec{K}_H \times \vec{\mathcal{H}}_H = -\nu \vec{D}_H \quad . \quad (3.12)$$

and

$$\vec{K}_H \times \vec{E}_H = \nu \mu_0 \vec{\mathcal{H}}_H \quad . \quad (3.13)$$

These two equations show that $\vec{K}_H$, $\vec{\mathcal{H}}_H$ and $\vec{D}_H$ form a mutually orthogonal set.

From Equations 3.4 and 3.7, Equation 3.10 for the displacement vector may be written in terms of $\vec{E}$ as

$$\sum_H \vec{D}_H \exp(-2\pi i \vec{K}_H \cdot \vec{r}) = \varepsilon_0 [1 - \Gamma \sum_{H'} F_{H'} \exp(-2\pi i \vec{H}' \cdot \vec{r})] \sum_H \vec{E}_H \exp(-2\pi i \vec{K}_H \cdot \vec{r}) \quad , \quad (3.14)$$

where the index H' is used to distinguish it from H . Since

$$\vec{K}_{H'} + \vec{H} = \vec{K}_{H'+H} \quad , \quad (3.15)$$

Equation 3.14 can be written

$$\sum_H \vec{D}_H \exp(-2\pi i \vec{K}_H \cdot \vec{r}) = \varepsilon_0 \sum_H \vec{E}_H \exp(-2\pi i \vec{K}_H \cdot \vec{r}) - \varepsilon_0 \Gamma \sum_H (\sum_P F_{H-P} \vec{E}_P) \exp(-2\pi i \vec{K}_H \cdot \vec{r}) \quad , \quad (3.16)$$

after changing the indices of summation [23]. This equation is valid for all positions, $\vec{r}$, and for all Fourier components, so

$$\vec{D}_H = \varepsilon_0 \vec{E}_H - \varepsilon_0 \Gamma \sum_P F_{H-P} \vec{E}_P = \varepsilon_0 (1 - \Gamma F_0) \vec{E}_H - \varepsilon_0 \Gamma \sum_{P \neq H} F_{H-P} \vec{E}_P \quad . \quad (3.17)$$

The displacement field is thus dominated by $\varepsilon_0 \kappa_0 \vec{E}_H$, where $\kappa_0 \equiv 1 - \Gamma F_0$, but contains small contributions from other Fourier components of the electric field.

Taking the cross product of $\vec{K}_H$ with each side of Equation 3.9 and substituting in Equation 3.8,

$$\vec{K}_H \times (\vec{K}_H \times \vec{E}_H) = \nu \mu_0 (\vec{K}_H \times \vec{H}_H) = -\nu^2 \mu_0 \vec{D}_H . \quad (3.18)$$

Using the form of the displacement in Equation 3.17, this becomes

$$\vec{K}_H \times (\vec{K}_H \times \vec{E}_H) = -\nu^2 \mu_0 \varepsilon_0 (\vec{E}_H - \Gamma \sum_P F_{H-P} \vec{E}_P) . \quad (3.19)$$

The vacuum value of the wavevector is related to the frequency by $k = \nu/c$, and since $\mu_0 \varepsilon_0 = 1/c^2$,

$$\vec{K}_H \times (\vec{K}_H \times \vec{E}_H) + k^2 \vec{E}_H - k^2 \Gamma \sum_P F_{H-P} \vec{E}_P = 0 . \quad (3.20)$$

Using the vector identity for the triple cross product, this becomes

$$[k^2(1 - \Gamma F_0) - (\vec{K}_H \cdot \vec{K}_H)] \vec{E}_H - k^2 \Gamma \sum_{P \neq H} F_{H-P} \vec{E}_P + (\vec{K}_H \cdot \vec{E}_H) \vec{K}_H = 0 . \quad (3.21)$$

This set of equations completely describes the electromagnetic field inside the crystal [23]. This is a complex vector equation for each amplitude, $\vec{E}_H$, and must hold for the real and imaginary parts, and for each component of the vectors separately.

If only one reciprocal lattice point, $\vec{H}$, is near enough to the Ewald sphere to give any appreciable diffraction, we can neglect all field amplitudes except $\vec{E}_0$ and $\vec{E}_H$. Bragg's law defines the plane of incidence as that containing the wavevectors $\vec{K}_0$ and $\vec{K}_H$. The components of $\vec{E}_0$ and $\vec{E}_H$ may then be described by components parallel or perpendicular to this plane. The perpendicular component is called the σ -polarization, after the german word "senkrecht" for "perpendicular". The component in the diffraction plane is called the π -polarization.

For the σ -polarization state Equation 3.21 gives

$$[k^2(1 - \Gamma F_0) - (\vec{K}_0 \cdot \vec{K}_0)] E_0^\sigma - k^2 \Gamma F_H E_H^\sigma = 0 , \quad (3.22)$$

and

$$-k^2 \Gamma F_H E_0^\sigma + [k^2(1 - \Gamma F_0) - (\vec{K}_H \cdot \vec{K}_H)] E_H^\sigma = 0 . \quad (3.23)$$

Nontrivial solutions to this pair of equations for the ratio E_H^σ/E_0^σ requires that the determinant be zero. To generalize the relation for either polarization we let $P = 1$, for the σ polarization, and $P = \cos 2\theta$, for the π polarization. The following determinant must then equal zero for either value of P

$$\begin{vmatrix} k^2(1 - \Gamma F_0) - \vec{K}_0 \cdot \vec{K}_0 & -k^2 P \Gamma F_H \\ -k^2 P \Gamma F_H & k^2(1 - \Gamma F_0) - \vec{K}_H \cdot \vec{K}_H \end{vmatrix} \quad (3.24)$$

Here k is the vacuum wavevector, $\vec{K}_0$ and $\vec{K}_H$ are the wavevectors in the material, and F_0 , F_H , F_H are the structure factors for the 0, H , and $\bar{H}$ reflections. The diagonal elements of the matrix represent the difference between the squares of the wavevectors $\vec{K}_0$ and $\vec{K}_H$ inside the crystal and the square of the vacuum wavevector, corrected for the average value of the dielectric constant, $(1 - \Gamma F_0)$. As a result, the index of refraction for the incident and diffracted waves is different from the average index of refraction (Figure 3.2).

Figure 3.2: The Ewald sphere in reciprocal space, showing the wavevector corrected by the average index of refraction. The Laue point, C , represents the centre of the sphere in vacuum, while Q is the centre in the real crystal.

Defining the difference parameters, ξ_0 and ξ_H , as

$$2k\xi_0 \equiv \vec{K}_0 \cdot \vec{K}_0 - k^2(1 - \Gamma F_0) , \quad (3.25)$$

and

$$2k\xi_H \equiv \vec{K}_H \cdot \vec{K}_H - k^2(1 - \Gamma F_0) \quad , \quad (3.26)$$

the fundamental equation for the dispersion surface is found,

$$\xi_0 \xi_H = \frac{1}{4} k^2 P^2 \Gamma^2 F_H F_{\bar{H}} \quad . \quad (3.27)$$

This is the fundamental result of the DTXRD [23]. It defines a constant energy surface which is the X-ray analog of the Fermi surface in the electron band theory of solids. As a consequence of this relation, it is found that the DTXRD changes the concept of the Ewald sphere. In reciprocal space there is no longer a single Ewald sphere for a single monochromatic incident ray. The dispersion surface defined by Equation 3.27 defines the loci of all permitted Ewald spheres. Wavevectors from points on this surface to points in the reciprocal lattice represent wave solutions to Maxwell's equations.

In the usual case, Figure 3.1, the distance from the centre, C , of the Ewald sphere to the origin and to a reciprocal lattice point, (HKL) is equal to the vacuum wavevector, k . The dynamical framework takes into account the average index of refraction inside the material, $\vec{k}(\text{inside}) = k(1 - \frac{1}{2}\Gamma F_0)$, with the result that the centre of the Ewald sphere is now at point Q as shown in Figure 3.2.

The boundary conditions for the field and wave vectors can now be applied in order to find solutions for a particular experimental geometry. The direction cosines of the incident and diffracted beams with respect to the incident crystal surface are given by $\vec{n} \cdot \vec{s}_0 = \gamma_0$ and $\vec{n} \cdot \vec{s} = \gamma_H$, where $\vec{n}$ is an inward unit vector and $\vec{s}_0$ and $\vec{s}$ are unit vectors in the incident and diffracted beam directions.

The dispersion parameters are found to be [23]

$$\xi_0 = \frac{1}{2} k \mid P \mid b \mid^{1/2} \Gamma [F_H F_{\bar{H}}]^{1/2} [\eta \pm (\eta^2 + b / \mid b \mid)^{1/2}] \quad , \quad (3.28)$$

and

$$\xi_H = \frac{1}{2} k \mid P \mid (\Gamma / \mid b \mid^{1/2}) [F_H F_{\bar{H}}]^{1/2} [\eta \pm (\eta^2 + b / \mid b \mid)^{1/2}]^{-1} \quad , \quad (3.29)$$

where $b \equiv \gamma_0 / \gamma_H$ and

$$\eta \equiv \frac{[b \Delta \theta \sin 2\theta_B + \frac{1}{2} \Gamma F_0 (1 - b)]}{\Gamma \mid P \mid b \mid^{1/2} [F_H F_{\bar{H}}]^{1/2}} \quad . \quad (3.30)$$

Figure 3.3: Shape of the (004) symmetric Bragg reflection for a GaAs crystal. The upper dotted curve is for zero absorption (Darwin curve) and the lower curve includes the absorption (Darwin-Prins curve).

To determine the ratio of the diffracted and incident electric field amplitudes for polarization P , from Equations 3.22 and 3.23, from the analogous relations for the π -polarization, and from the definitions of the difference parameters.

$$\frac{E_H}{E_0} = \frac{-2\xi_0}{kP\Gamma F_H} = \frac{-kP\Gamma F_H}{2\xi_H} . \quad (3.31)$$

In this thesis we consider the symmetric Bragg case, in which $b = -1$, where the diffracted beam exits from the same face of the crystal that the incident beam enters and at the same angle with respect to the surface. The form of the reflectivity curve in this geometry was derived by Darwin [28]. In this case the incident amplitudes inside and outside the crystal are the same, and the outside diffracted amplitude is equivalent to the inside diffracted field at the surface. Thus the diffracted beam is a

reflection. Multiplying the two expressions in Equation 3.31, we find

$$\left(\frac{E_H}{E_0}\right)^2 = \frac{\xi_0 F_H}{\xi_H F_H} = |b| (\eta \pm (\eta^2 - 1)^{1/2})^2 \frac{F_H}{F_H} . \quad (3.32)$$

The magnitude of this expression is the reflectivity which can be measured experimentally,

$$R = \left| \frac{F_H}{F_H} \right| |b| |\eta \pm (\eta^2 - 1)^{1/2}|^2 . \quad (3.33)$$

The sign to be chosen is opposite in sign to $\text{Re}(\eta)$, and is chosen to keep $R < 1$. When the crystal absorption is taken into account [29], a plot of the reflectivity versus the deviation from the Bragg angle, $\Delta\theta = \theta - \theta_B$, is known as the Darwin-Prins curve, or crystal rocking curve.

The reflectivity curve for a GaAs crystal with $(HKL)=(004)$ is shown in Figure 3.3 for Cu- K_{α_1} X-rays ($\lambda = 1.54061$ Å). The effect of the crystal absorption is seen in the figure, from which it is apparent that the absorption is more pronounced at the high angle side. This is a manifestation of the standing waves due to the interference field which is produced in the crystal. Having now reviewed the fundamental results of the DTXRD we consider the standing wave phenomenon in the next section.

3.2 X-Ray Standing Waves

The interference of the incident and diffracted waves in a perfect crystal produces a standing wave pattern as a consequence of the dynamical nature of the interaction and was discussed in the thorough review by Batterman and Cole [23]. Following the experimental observation [30] of fluorescence scattering by foreign atoms (As) in a silicon crystal associated with the standing wave field, the technique has found widespread application in many areas of surface science. The use of synchrotron radiation has made measuring times reasonable, reduced the effects of the dispersiveness of crystal arrangements, and allowed a wide range of X-Ray energies to be employed. This section reviews the principles of the XSW technique, particularly those aspects which enable the measurement of δ -layers embedded in epitaxial semiconductors.

3.2.1 Principles of the XSW Technique

An outstanding XSW review by Zegenhagen [31] covers the important theoretical and practical aspects of the technique, especially for the evaluation of adsorbate species on crystal surfaces. A feature of XSW for the study of adsorbates or buried impurities in crystals is that the technique is element-specific, thus atomic distributions may be detected individually, and positional information may be obtained with an accuracy of 0.01 Å under favourable conditions. However, it must be verified that the measured signal is actually originating from the atoms under consideration.

The formalism for XSW structural analysis was developed by Hertel *et al.*[32]. They recognized that analyzing a distribution of atoms with XSW and diffraction vector $\vec{H}$ is equivalent to determining the amplitude, F^H , and phase, P^H , of the $\vec{H}$ th Fourier component of the atomic distribution function.

X-ray standing waves are generated by the superposition of two coherently related travelling waves. We assume that the waves are planar and linearly polarized and that the electric field vectors of both waves are parallel. We will restrict our attention to the σ -polarization which is most commonly used. Representing the incident and reflected waves by their complex amplitudes, $\mathcal{E}_0$ and $\mathcal{E}_H$, respectively, we have [31]

$$\mathcal{E}_0 = E_0 \exp[2\pi i(\nu_0 t - \vec{K}_0 \cdot \vec{r})] \quad , \quad (3.34)$$

and

$$\mathcal{E}_H = E_H \exp[2\pi i(\nu_H t - \vec{K}_H \cdot \vec{r})] \quad , \quad (3.35)$$

where $\nu_0 = \nu_H = \nu$ is the frequency of the radiation, and $\vec{r}$ is a coordinate vector relative to an arbitrary origin. Bragg's law relates the incident, $\vec{K}_0$, and diffracted, $\vec{K}_H$, wavevectors as $\vec{K}_H = \vec{K}_0 + \vec{H}$, in terms of the diffraction vector, $\vec{H}$, where $|\vec{K}_H| = |\vec{K}_0|$. Assuming $\mathcal{E}_0$ and $\mathcal{E}_H$ are coherent, the (complex) amplitudes E_0 and E_H are related via the phase factor α as

$$E_H = \sqrt{R} E_0 \exp(i\alpha) \quad . \quad (3.36)$$

Here R and α denote the intensity and the phase of the reflected wave relative to the incident wave, respectively, where the reflectivity is determined from the DTXRD (Section 3.1).

Superposition of the two waves yields an expression [31] for the intensity of the interference field in terms of the total field,

$$\mathcal{E} = \mathcal{E}_H + \mathcal{E}_0 \quad , \quad (3.37)$$

as

$$\mathcal{E}\mathcal{E}^*/\|E_0\|^2 = I = 1 + R + 2\sqrt{R}\cos(\alpha - 2\pi\vec{H} \cdot \vec{r}) \quad . \quad (3.38)$$

It is convenient to discuss the reflectivity in terms of the quantity η (c.f. Equation 3.30) for generality. Note that low values of η correspond to high values of $\Delta\theta$ and vice-versa. As the incident X-ray energy moves from the high η side of the Bragg peak to the low η side, the phase of the wavefield changes continuously by π , i.e.,

$$\begin{aligned} \alpha &= \phi \quad , \quad \text{for } \text{Re}(E_H/E_0) > 0 \quad , \\ \alpha &= \phi + \pi \quad , \quad \text{for } \text{Re}(E_H/E_0) < 0 \quad , \end{aligned} \quad (3.39)$$

where

$$\phi = \tan^{-1} \left[\frac{\text{Im}(E_H/E_0)}{\text{Re}(E_H/E_0)} \right] \quad . \quad (3.40)$$

These expressions describe the spatial modulation of the wavefield [31]. A standing wave is produced in the crystal with maxima and minima lying on planes in the direction normal to $\vec{H}$. At the high η side of the Bragg reflection the nodes of the XSW lie on the substrate planes. As the phase changes in the region of the Bragg peak the wavefield moves continuously until the antinodes lie on the substrate planes at the low η side.

Notice that Equation 3.38 does not depend on time. The intensity of the wavefield is spatially modulated since $\vec{H} \cdot \vec{r}$ is a dimensionless, real number. In the direction of $\vec{H}$ the intensity modulation is maximum and zero in the direction normal to $\vec{H}$. Minima (nodes) and maxima (antinodes) of the wavefield lie on planes. Thus the superposition of the two coherent plane waves $\mathcal{E}_0$ and $\mathcal{E}_H$ creates a planar interference field in the crystal.

The detection of the XSW intensity at the location of a particular atomic species requires the measurement of some property which is proportional to that intensity.

In the X-Ray energy range the important inelastic X-Ray scattering process is photoabsorption. Here a photon with energy E_γ is completely absorbed and

$$E_\gamma = E_f - E_i \quad , \quad (3.41)$$

where E_f and E_i are the binding energies of the final (excited) and initial states of the electron, respectively. The electron is excited into empty states above the Fermi level, in the same manner as occurs in the XAFS technique (Chapter 4). It is assumed that the scattering probability and thus the scattered intensity, I_{sc} , is a linear function of the X-Ray intensity at the position of the scatterer [31].

From Figure 3.4 it is apparent that for a given plane spacing, d_s , moving the standing wave in a controlled way allows a measurement of the distance between A and B along z , by determining how much the wavefield must shift in order to observe maximum scattering from A or B. Figure 3.4 also shows that this distance can only be determined *modulo* d_s .

Figure 3.4: Schematic of the XSW technique. Maximum fluorescence from a particular atomic species is observed when the antinodal planes pass through the atoms. The fluorescence emission is characteristic of the absorbing atoms.

The wavefield given by Equation 3.38 has a spacing, d_s , determined by the relationship between the propagation vectors $\vec{k}_0$ and $\vec{k}_H$. Denoting the z -coordinate

parallel to $\vec{H}$ as z_H , where $H = |\vec{H}|$, we have [31]

$$\vec{H} \cdot \vec{r} = Hz_H \quad . \quad (3.42)$$

The period of the cosine function in Equation 3.38 is $Hd_s = 1$, thus the spacing, d_s , between the wavefield maxima is

$$d_s = H^{-1} = |\vec{K}_H - \vec{K}_0|^{-1} \quad . \quad (3.43)$$

From Bragg's law,

$$d_s = H^{-1} = \frac{1}{2}\lambda(\sin\theta)^{-1} \quad , \quad (3.44)$$

and so the smallest spacing, $d_{s,min}$, of the wavefield is

$$d_{s,min} = \frac{\lambda}{2}, \quad \text{for } \theta \approx 90^\circ \quad . \quad (3.45)$$

Similarly, the wavefield spacing increases as θ approaches zero,

$$d_{s,max} \rightarrow \infty, \quad \text{for } \theta \rightarrow 0 \quad . \quad (3.46)$$

By adjusting $\vec{H}$ or θ it is thus possible to adjust the wavefield spacing to the scale of a given structural problem.

Of the experimental geometries producing standing waves in crystals the Bragg case is the most useful and the only one in the present discussion. The total reflection geometry near $\theta = 0$ can also be formally considered as a 0th order Bragg reflection and is discussed in Section 4.3.3. Scanning through the Bragg condition in a crystal is accomplished by varying the parameter η . A traditional setup involves a rocking curve measurement in which the angle of incidence, θ , of the X-Ray beam is varied throughout the angular range of the Bragg reflection. This geometry will be discussed in detail in connection with the experimental HRXRD studies described in Section 6.5.

It has been noted [33], however, that for the Bragg case close to $\theta = 90^\circ$ the variable parameter of Equation 3.30 may be rewritten

$$\eta = \frac{(-2\Delta E/E + \Gamma F_0)}{\Gamma[F_H F_H]^{1/2}} \quad . \quad (3.47)$$

Passing through the range of the Bragg reflection, the phase, α , changes by π and the XSW field moves half a diffraction plane spacing. This can be achieved by tuning η either using the angle, θ , or the energy, E . In the case of noticeable absorption the phase change of exactly π can only be achieved by extending the angular range far beyond the width of the Bragg reflection region.

The orientation of the wavefield pattern is determined [31] by the diffraction vector, $\vec{H}$. When $\vec{H}$ is oriented normal to the crystal surface the wavefield planes are oriented parallel to the surface. Other orientations can also be employed, provided the diffracted wave appears at the same crystal face as the incident wave. Several measurements using different reflections can be useful in realizing a complete structural analysis. Figure 3.5 shows the reflectivity, R , the phase, α , and the wavefield intensity, I , for several positions $\vec{r}$ relative to the (004) planes of a (001)-oriented GaAs crystal in the backreflection geometry.

The total reflection range of a symmetric Bragg reflection of σ -polarized X-Rays has a width

$$W_\theta = \frac{2\Gamma(F_H F_{\bar{H}})^{1/2}}{\sin(2\theta_B)} . \quad (3.48)$$

This result is derived from Equation 3.30, and corresponds to a range of $\eta' = -1$ to $\eta' = +1$, where $\eta' = \eta - F_0/(F_H F_{\bar{H}})^{1/2}$. For example, the GaAs(004) rocking curve shown in Figure 3.3 for the case of no absorption has $W_\theta = 8.2$ arcsec. As the incidence angle is increased $\sin(2\theta_B)$ becomes very small and the angular range increases steeply [33]. In the back-reflection mode ($\theta_B \approx 90^\circ$), Equation 3.30 no longer applies, nor does Equation 3.48. If the rocking curve is scanned in energy, however, as suggested by Equation 3.47, then the rocking curve width is increased strongly. In energy, the back-reflection rocking curve has a total reflection width given by $W_E = E\Gamma(F_H F_{\bar{H}})^{1/2}$. Note that the back-reflection geometry restricts the choice of wavelengths to those for which $\lambda = 2d_s$.

The experimental details describing the use of back-reflection XSW will be presented in Chapter 6.6. In the following section the methods for interpreting XSW data are described.

Figure 3.5: (a) Reflectivity, R , and phase, α , of the symmetric GaAs(004) back-reflection. (b) Reflectivity and XSW intensities for different values of $H z_H$ within the GaAs unit cell, as indicated.

3.2.2 XSW Analysis

As discussed in Section 3.2.1 the intensity of the XSW wavefield at the location of a given atom is given by the expression

$$I = 1 + R + 2\sqrt{R}\cos(\alpha - 2\pi\vec{H} \cdot \vec{r}) . \quad (3.49)$$

In practice, the measurement is made by monitoring an emission channel which is proportional to this intensity. Fluorescence emission has been used exclusively in this work, although the measurement of photoelectrons or Auger electrons are also common. In these cases, XSW is complemented by X-Ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), respectively.

The measurement of the atomic fluorescence as the XSW emission channel requires the use of the dipole approximation [31]. In practice, the quadropole contribution to the absorption cross-section is small and the dipole approximation is adequate. The use of the fluorescence channel combines the XSW technique with the features of energy-dispersive X-Ray spectroscopy (EDX).

An XSW measurement samples the fluorescence from all of the atoms of the species of interest within the crystal [31]. For N atoms, with positions denoted by $\vec{r}_i$, the scattered yield is

$$Y^H = 1 + R + 2\sqrt{R}N^{-1} \sum_{i=1}^N \cos(\alpha - 2\pi\vec{H} \cdot \vec{r}_i) . \quad (3.50)$$

This can be expressed in terms of a distribution function $G(\vec{r})$, where

$$Y^H = 1 + R + 2\sqrt{R} \int_V G(\vec{r}) \cos(\alpha - 2\pi\vec{H} \cdot \vec{r}) d\vec{r} , \quad (3.51)$$

and $\int_V G(\vec{r}) d\vec{r} = 1$. Here the integral is taken over the volume, V , containing the X-Ray interference field.

The component of $\vec{r}_i$ parallel to $\vec{H}$ is z_i^H , where

$$\vec{H} \cdot \vec{r}_i = |\vec{H}| z_i^H = P_i^H . \quad (3.52)$$

The position of the atom of interest with respect to the diffraction planes of the substrate is given by P_i^H , where $0 \leq P_i^H < 1$. Thus P_i^H measures the position of a

given atomic species relative to a diffraction plane of the set $\vec{H}$, normalized by the plane spacing, d_s . Note that P_i^H is actually determined *modulo*- d_s , so that values of e.g. 0.15 and 1.15 are equivalent. With this notation, Equation 3.51 may be rewritten

$$Y^H = 1 + R + 2\sqrt{R}F^H \cos(\alpha - 2\pi P^H) . \quad (3.53)$$

The parameters P^H and F^H are called the coherent position and coherent fraction, respectively [31]. If the atomic species under consideration occupy n positions (P_i^H) relative to the diffraction planes, then P^H and F^H may be written [32]

$$F^H = A_s^H \equiv (G_H^c{}^2 + G_H^s{}^2)^{1/2} , \quad (3.54)$$

and

$$P^H = \frac{1}{2\pi} \tan^{-1}\left(\frac{G_H^s}{G_H^c}\right) + \begin{cases} 0.5 & \text{if } G_H^c < 0 \\ 0 & \text{otherwise} \end{cases} . \quad (3.55)$$

where the cosine term, G_H^c , is

$$G_H^c = \sum_{i=1}^n c_i \cos(2\pi P_i^H) , \quad (3.56)$$

and the sine term, G_H^s , is

$$G_H^s = \sum_{i=1}^n c_i \sin(2\pi P_i^H) . \quad (3.57)$$

The coefficients in these expressions satisfy the normalization $\sum_{i=1}^n c_i = 1$, where c_i denotes the relative population of the position P_i^H .

Thermal vibrations may be taken into account by convolution of $G(\vec{r})$ with a normalized Gaussian distribution:

$$G_G(\vec{r}) = \frac{1}{\sqrt{2\pi}\sigma_H} \exp\left[-\frac{z_R^2}{2\sigma_H^2}\right] , \quad (3.58)$$

where

$$\sigma_H^2 = \langle u_H^2 \rangle H^2 . \quad (3.59)$$

Here $z_R \equiv \Delta d/d_H$ where Δd is the displacement of the atom from the diffraction planes. The mean-square vibrational amplitude of the atoms in the direction of $\vec{H}$ is $\langle u_H^2 \rangle$.

Now, the coherent fraction including the thermal disorder is [31]

$$F^H = A_s^H D^H \quad , \quad (3.60)$$

where the Debye-Waller factor is $D^H = e^{-M}$ and $M = 2\pi^2 \langle u_H^2 \rangle > H^2$. Note that the coherent position is unaffected by the thermal disorder. Very careful diffraction studies [34] have established that the room temperature Debye-Waller factor for the GaAs (004)-reflection has a value of ~ 0.9 .

In this section the method of XSW analysis has been presented in a manner which permits the interpretation of the experimental data for layers of InAs embedded in GaAs, as will be discussed. In the following section the DTXRD framework described in an earlier section is extended to allow the interpretation of diffraction data from layered semiconductor heterostructures.

3.3 Simulation of X-Ray Rocking Curves

As mentioned in the introduction to this chapter, the analysis of high-resolution X-Ray diffraction data relies upon the solution to the so-called Takagi-Taupin equations. A treatment of this subject is now presented which leads to the elegant form of solution derived by Bartels *et al.* [17].

The X-Ray diffraction theory for crystals with a strain gradient perpendicular to the surface was developed by Takagi [25] and independently by Taupin [26] shortly thereafter. According to Taupin, the system of equations may be written as

$$i \frac{\lambda \gamma_H}{\pi} \frac{dD_H}{dz} = \Psi_0 D_H + \Psi_H D_0 - \alpha_H D_H \quad , \quad (3.61)$$

and

$$i \frac{\lambda \gamma_0}{\pi} \frac{dD_0}{dz} = \Psi_0 D_0 + \Psi_H D_H \quad . \quad (3.62)$$

Here D_0 and D_H are the amplitudes of the incident and diffracted waves at the depth z in the crystal. The direction cosines are γ_0 and γ_H , and λ is the X-Ray wavelength in vacuum. The quantities Ψ_0 and Ψ_H are related to the structure factors of the material at the depth z as $\Psi_0 = -(\lambda^2 r_e / \pi V) F_0$ and $\Psi_H = -(\lambda^2 r_e / \pi V) F_H$, where r_e

is the classical electron radius as defined in section 3.1. Taupin defined

$$\alpha_H = \lambda^2 \left(\frac{1}{d_H^2} - \frac{2\sin\theta_B}{\lambda d_H} \right) , \quad (3.63)$$

where d_H is the diffraction plane spacing at the depth z . Denoting the amplitude ratio by $X = D_H/D_0$, the system of equations may be combined to give [35]

$$\frac{dX}{dz} = \frac{i\pi}{\lambda \sin\theta_B} \left[\Psi_H X^2 + 2\Psi_0 - \alpha_H(z)X + \Psi_H \right] . \quad (3.64)$$

Here the quantity $\alpha(z)$ takes into account the deviation from the exact Bragg condition,

$$\alpha_H(z) = \alpha_H(0) + \Delta\alpha_H(z) , \quad (3.65)$$

where $\alpha_H(0)$ is the deviation of the incident angle from the substrate Bragg angle, and $\Delta\alpha_H(z)$ is the additional deviation due to the presence of impurities in the crystal (or epitaxial heterolayers). With this formulation the equations were solved numerically, using the Runge-Kutta method [35]. In this way Burgeat and Taupin were able to determine the diffusion coefficient of boron in silicon from experimental XRD profiles.

In the SFU MOVPE laboratory a commercial software package is used for the simulation of rocking curves from III-V heterostructures.¹ The program employs a solution to the Takagi-Taupin equations derived by Halliwell *et al.* [36] and Hill *et al.* [37]. A shortcoming of the algorithm described in these articles is that the relationship with the Darwin-Prins formula (Equation 3.33) for an infinitely thick, absorbing, perfect crystal is not transparent. Moreover, details of the method are omitted from these articles, perhaps for proprietary reasons.

Bartels *et al.* [17] developed a recursive method of solution based on Taupin's single differential equation for the Bragg case,

$$-i \frac{dX}{dT} = X^2 - 2\eta X + 1 , \quad (3.66)$$

where

$$X = \left(\frac{F_H}{F_0} \right)^{1/2} \left| \frac{\gamma_H}{\gamma_0} \right|^{1/2} \frac{D_H}{D_0} , \quad (3.67)$$

¹RADS: Rocking Curve Analysis by Dynamical Simulation, BEDE SCIENTIFIC, UK

and

$$T = \frac{\pi P \Gamma (F_H F_H)^{1/2} t}{\lambda |\gamma_0 \gamma_H|^{1/2}} . \quad (3.68)$$

The quantity η and other values are defined as in Section 3.1. The layer thickness, t , and the structure factor, F_H , are used to evaluate the quantity, T . The differential equation (3.66) can then be solved for layers of constant η and arbitrary thickness [17]. Recursion relations are used to describe the amplitude ratio at the bottom of a given layer, X_0 , to the amplitude ratio at the top, X_t .

Figure 3.6: The recursion method involves adding a layer of thickness t to the substrate so that the reflected amplitude at the surface changes from X_0 to X_t .

Now,

$$X_t = \eta + (\eta^2 - 1)^{1/2} \left[\frac{(S_1 + S_2)}{(S_1 - S_2)} \right] , \quad (3.69)$$

where

$$S_1 = [X_0 - \eta + (\eta^2 - 1)^{1/2}] \exp[-iT(\eta^2 - 1)^{1/2}] , \quad (3.70)$$

and

$$S_2 = [X_0 - \eta - (\eta^2 - 1)^{1/2}] \exp[iT(\eta^2 - 1)^{1/2}] . \quad (3.71)$$

These relations describe the general solution for the dynamical reflection of an epitaxial layer of arbitrary thickness [17], and allow the calculation of rocking curves of complicated layer structures. For an infinitely thick crystal the result reduces to the Darwin-Prins formula (Equation 3.33). In the calculation the reflected amplitude

deep within the substrate is taken to be zero. Figure 3.3 illustrates the situation for a single layer and a substrate. In the figure X_R and X_T are the reflected and transmitted amplitude ratios for the epitaxial layer.

To demonstrate the use of this method, Figure 3.7 shows the results obtained using the recursion relations for structures of interest to this thesis. In the bottom part, a single ML of InAs deposited on GaAs(001) and buried by 100 Å of GaAs is considered using the GaAs(004) symmetric reflection, with σ -polarized Cu-K $_{\alpha 1}$ X-Rays. The top part shows a superlattice structure, in which the (1 ML InAs/ 100 Å GaAs) growth sequence is repeated 35 times. It is apparent that the present method of simulation agrees very well with the results obtained using the commercial software. The small discrepancies may arise because the commercial package neglects the volume change (and hence the change in susceptibility) which occurs in strained epitaxy, and because of small differences between the material parameters used in the two programs.

This chapter has described the principles of the diffraction-based techniques employed in this work. In the following chapter the XAFS technique will be discussed. These long-range order and short-range order techniques complement one another in the measurements of semiconductor heterostructures studied in this thesis.

Figure 3.7: Simulated X-Ray rocking curves for a GaAs(001)/1 ML InAs/100 Å GaAs structure (bottom) and for a $35 \times (1 \text{ ML InAs}/100 \text{ Å GaAs})$ superlattice on GaAs(001) (top). The simulations were carried out in the neighbourhood of the (004) substrate reflection in the σ -polarization. The top curve in each part illustrates the results obtained using the RADS package. The curves were offset for clarity.

Chapter 4

X-Ray Absorption Fine Structure

In this chapter the principles of the XAFS technique will be described. First a general, conceptual description of the phenomenon will be presented. The mathematical expression for the process in the extended regime will be given in a form which includes the polarization dependence, of interest in the measurement of oriented (semiconductor) samples. Finally the glancing incidence measurement geometry and the calculation of reflectivity curves for layered samples will be discussed.

4.1 Principles of XAFS

XAFS refers to the structure which appears in the absorption coefficient of atoms in condensed matter during the absorption of X-Ray photons from a synchrotron source, for example. This consists of two regimes. In the neighbourhood of the absorption edge, the X-Ray absorption near edge structure (XANES) is observed. For increasing photon energies, the extended X-Ray absorption fine structure (EXAFS) appears. It is the latter which is primarily of interest to this thesis, although the “extended” qualifier is often omitted. Excellent reviews are available in the literature [38], including a review of very recent developments by Crozier [39].

X-Ray photons are absorbed by atoms when the X-Rays are sufficiently energetic to free a bound electron in the atom [40]. When the electrons are in the most tightly bound ($n=1$) shell, the edge is called the K-edge. For the next most tightly bound

electrons the edge is known as the L-edge, and so on. For photon energies up to about 40 keV the incident photon is completely absorbed, transferring its energy to excite a photoelectron and leaving behind a core hole. In the measurements described in this thesis, the hole is subsequently filled by an electron in a higher shell with the emission of a fluorescence photon. By monitoring the fluorescence emission of the absorbing species it is possible to measure quantitatively the absorption coefficient of these atoms.

If all of the absorbed photon's energy is used to excite the core electron then the kinetic energy of the photoelectron is given by the difference between the incident photon energy and the binding energy of the electron in the atom [40]. From the deBroglie relation the momentum of the outgoing photoelectron is $p = h/\lambda$, in terms of the wavelength, λ and Planck's constant, h . The momentum is given by

$$\frac{p^2}{2m} = h\nu - E_0 \quad . \quad (4.1)$$

where ν is the frequency of the X-Ray photon and E_0 is the binding energy of the photoelectron.

XAFS does not occur for isolated atoms. In such a situation the absorption is a smooth function of energy above the absorption edge. For an absorbing atom surrounded by some arrangement of neighbouring atoms, the outgoing photoelectron wave is scattered by those neighbours. Figure 4.1 shows such an arrangement for the first coordination shell of an atom in the zincblende lattice. The final state consists of the superposition of the outgoing and scattered waves.

Quantum mechanically the absorption process is described by Fermi's Golden Rule [41]. The transition rate depends on the dipole operator and may be written

$$W_{i \rightarrow f} = \left(\frac{2\pi}{\hbar} \right) \left(\frac{e\mathcal{E}_0}{2} \right)^2 |\langle f | z | i \rangle|^2 \rho(E_f) \quad . \quad (4.2)$$

Here $\rho(E_f)$ is the density of final states, the initial K-shell core state is $| i \rangle$ and the final state of the electron excited to the escaping photoelectron is $| f \rangle$. Their respective energies are E_i and $E_f = E_i + \hbar\omega$, where $\hbar\omega$ is the photon energy [40]. The electric field is denoted by $\mathcal{E}_0$ and is oriented along the z -direction.

Figure 4.1: The propagation of the spherical photoelectron wave (heavy dashed lines) excited from an atom in the zincblende lattice. Backscattering from the atoms in the first coordination shell (light lines), and higher shells to a lesser extent, leads to the oscillatory behaviour in the absorption coefficient.

The backscattered waves affect the outgoing wave at the centre of the absorbing atom by contributing a characteristic phase. The total amplitude of the electron wave function will be enhanced or reduced, causing a corresponding change in the probability of X-Ray absorption [40]. The oscillations, or fine structure above the absorption edge thus exhibits peaks when the backscattered wave is in phase with the outgoing wave, and valleys when the two are out of phase. These characteristics are apparent in Figure 4.2 which shows the K-edge XAFS for a GaAs powder sample.

The variation of the phase with the photoelectron energy depends on the distance between the absorber and the backscatterer. The variation in the amplitude of the backscattering as a function of energy depends on the type of backscatterer. Thus, in Figure 4.2 the XAFS contains element-specific information on the local environment of the Ga absorbing atoms. In the following section a mathematical expression is provided to permit the analysis of experimental data.

Figure 4.2: Ga K-edge XAFS from a GaAs powder sample. The data were obtained in transmission at beamline X23A2 at the NSLS.

4.2 The EXAFS Expression

When the energy of incident photons is increased through the absorption edge, the XAFS, $\chi(E)$ appears as an additional term in the absorption,

$$\mu(E) = \mu_0(E)(1 + \chi(E)) \quad , \quad (4.3)$$

where $\mu_0(E)$ is the absorption of an isolated atom. Rearranging, the fine structure is given by

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \quad . \quad (4.4)$$

The XAFS, $\chi(k)$, for K-edge absorption may be expressed as a function of photoelectron wavevector, $k = \sqrt{2m(E - E_0)}/\hbar$, as

$$\chi(k) = \sum_i B_i(k) \sin[2kR_i + 2\delta(k) + \phi_i(k)] \quad (4.5)$$

where the sum is taken over all atoms, i , located at distances R_i from the absorbing atom. Phase shifts, $\delta(k)$ and $\phi_i(k)$, arise from the interaction with the absorber and the backscatterer, respectively.

The amplitude function, $B_i(k)$, is

$$B_i(k) = \frac{N_i^*}{kR_i^2} S_0^2 F_i(k) e^{-2R_i/\lambda_i(k)} e^{-2k^2\sigma_i^2} \quad (4.6)$$

where

$$N_i^* = 3N_i \cos^2(\theta_i) \quad (4.7)$$

Here N_i is the number of atoms of type i located at an average distance R_i from the absorber. The factor $\cos^2(\theta_i)$ is related to the polarization dependence of the K-edge XAFS, where θ_i is the angle between the electric vector and the bond between the absorber and the backscatterer (recall that the absorption depends on the dipole operator, $\vec{\mathcal{E}} \cdot \vec{r}$). S_0^2 is the passive electron factor describing the overlap between the wavefunctions of the electrons in the absorbing atom before and after the ejection of the core photoelectron ($S_0^2 \leq 1$). The backscattering amplitude of atom i is given by $F_i(k)$, $e^{-2k^2\sigma_i^2}$ is the XAFS Debye-Waller factor where σ_i^2 is the mean-square relative displacement about the average distance R_i , including thermal and static disorder, and $\lambda_i(k)$ is the mean free path of the photoelectron [40].

Historically, XAFS data were analyzed by comparing the spectrum for the sample of interest to a reference compound (or several compounds) containing the same absorbing and backscattering species, approximately the same distance apart as in the unknown sample. In this method of analysis the XAFS appears as

$$\chi(k) = \frac{N_i}{kR_i^2} |f_i(k)| \sin[2kR_i + \phi_i(k)] \quad (4.8)$$

where the empirical phase, $\phi_i(k)$, and amplitude, $|f_i(k)|$ are determined from the standard sample. The data are then curve-fitted to determine the nearest neighbour distances, N_i , and the bond lengths, R_i .

The radial distribution function may be obtained by taking the Fourier transform of $\chi(k)$ [42]. The realization of this point constituted a major step in the development of modern XAFS. The functional form of the Fourier transform is

$$FT[k^p \chi(k)] = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} dk w(k) k^p \chi(k) e^{(2ikR_f)} \quad , \quad (4.9)$$

where k_{min} and k_{max} are the limits of the data and p is the power of the k -weighting used to emphasize a particular range of the spectrum. Due to the finite range of the data in k -space, a transform window, $w(k)$, is used to minimize transform artifacts. In this thesis a 10% Gaussian window was used, having the form

$$w(k) = \exp \left[\left(\frac{2(k - k_{mid})}{\Delta k} \right)^2 \ln(0.1) \right] \quad , \quad (4.10)$$

where the data are taken over the interval $\Delta k = k_{max} - k_{min}$, and k_{mid} is the midpoint of the range.

Recent developments have enabled the calculation of theoretical XAFS spectra for any arrangement of atoms, even those for which no reference compound exists [43]. An example of such a calculation package is FEFF6b which is used in this thesis [44]. Details of this method of data analysis appear in Chapter 7.7.

Having now reviewed the principles of XAFS, in the next section we address the details of the glancing incidence geometry used for polarization-dependent studies.

4.3 The Glancing Incidence Geometry

In the glancing (or grazing) incidence geometry, polarized photons from a synchrotron source are incident on a specimen at very shallow angles. The photon energy is then varied in the usual way to measure the XAFS. Surface or near-surface measurements are now routinely performed in this geometry with incident angles, θ , in the neighbourhood of the critical angle for total external reflection, θ_C . The theoretical basis for evaluating the electric field amplitudes within samples aligned in this geometry has been summarized by Jiang [45]. In this section an overview of the physics will be given in order to calculate the field intensities in layered semiconductor crystals.

4.3.1 Parratt's Formulation

A method for calculating the glancing incidence reflectivity in stratified, layered systems was developed by Parratt [46] some time ago. More recent theories have been published by Kohn [47] and others. In the present discussion the former approach will be used. Although Kohn's transfer matrix method is more elegant, the physical basis is the same.

Figure 4.3: The propagation of a plane wave in a layered structure. In this example layer 3 corresponds to the vacuum above the system, while the substrate is layer 0. Note that the electric field amplitudes refer to the values at the centre of each layer, while the z coordinate is also measured from the centre of the layer.

Consider a layered structure as shown in Figure 4.3. The substrate is taken as layer $m=0$, with increasing layer indices along the growth (-ve z) direction. For the system depicted here the vacuum space above the sample is denoted by $m=3$, with corresponding amplitudes E_3 and E_3^R for the incident and reflected electric field components, respectively. In the following discussion the σ -polarization will be assumed, although the same results are obtained for the π -polarization ($P=1$ for σ , and $P = \cos 2\theta_B \sim 1$ for π polarization with $\theta_B \sim 0$). The electric vector thus points out of the page in the y -direction.

In vacuum the wavevector, $\vec{k}$ is related to the frequency, ω , by $k = |\vec{k}| = \omega/c$. In a medium with complex index of refraction, n_i , the wavevector is $k_i = n_i\omega/c$. For the glancing incidence geometry the index of refraction is related to the (000) structure factor, F_0 . Including the dispersive, δ , and absorptive, β , parts of the index of refraction, we have

$$n = 1 - \delta - i\beta \quad , \quad (4.11)$$

where

$$\delta = \frac{1}{2}\Gamma F'_0 = \frac{1}{2}\lambda_0' = \frac{N_A}{2\pi} \frac{\epsilon^2}{mc^2} \frac{\rho}{M} \lambda^2 (f_0 + f') \quad , \quad (4.12)$$

and

$$\beta = \frac{1}{2}\Gamma F''_0 = \frac{1}{2}\lambda_0'' = \frac{N_A}{2\pi} \frac{\epsilon^2}{mc^2} \frac{\rho}{M} \lambda^2 (f'') \quad , \quad (4.13)$$

where F'_0 and F''_0 are the real and imaginary parts of the (000) structure factor with Γ as defined in Section 3.1. In the above, N_A is Avogadro's number, ρ is the mass density of the material with atomic weight M and λ is the X-Ray wavelength. In this discussion the layers are considered homogeneous, so that the only change in material occurs along the z -direction, perpendicular to the surface. The critical angle is determined from the relation $\theta_C = \sqrt{2\delta}$.

For a monochromatic, plane X-Ray wave incident on the system with wavevector $\vec{k}$ in the x, z -plane the wave is reflected and refracted at the boundaries. Thus, both refracted and reflected plane waves propagate in each layer. It is assumed that these are the only two such waves in the material. For the substrate (assumed infinitely thick) no reflected beam propagates. Within each layer the x -components of the two waves are the same, while the z -components have opposite signs. The tangential components, k_x , of the wavevectors are equal on either side of a boundary, while the z -components are different in the different media due to the different electric susceptibilities.

The electric field vector in layer m is written [45]

$$\vec{E}_m(x, z, t) = E(x, t) [\vec{E}_m \exp(-ik_{z_m} z) + \vec{E}_m^R \exp(ik_{z_m} z)] \quad , \quad (4.14)$$

where $E(x, t) = \exp[i(\omega t - k_x x)]$. Here $\vec{E}_m$ and $\vec{E}_m^R$ are the amplitudes of the refracted and reflected waves in the middle of the layer and the coordinate z is measured from the middle of the layer.

For a small angle of incidence, θ , at the top interface the wavevector may be approximated by $k_{z_3} \approx k_3$, and so

$$k_{z_2} \approx k_3(\theta^2 - 2\delta_2 - 2i\beta_2)^{1/2} . \quad (4.15)$$

Using the notation

$$f_m = (\theta^2 - 2\delta_m - 2i\beta_m)^{1/2} , \quad (4.16)$$

the general relationship between the wave number of the m th layer and that of vacuum is

$$k_{z_m} = k_3 f_m . \quad (4.17)$$

In the m th layer, the refracted beam is now

$$E_m(z_m) = E_m(0) \exp[i(\omega t - k_{x_m} x_m)] \exp(-ik_3 f_m z_m) . \quad (4.18)$$

The conditions of continuity for the electric and magnetic fields at the boundary between layers m and $m - 1$ can be written

$$a_m E_m + a_m^{-1} E_m^R = a_{m-1}^{-1} E_{m-1} + a_{m-1} E_{m-1}^R , \quad (4.19)$$

and

$$(a_m E_m - a_m^{-1} E_m^R) f_m = (a_{m-1}^{-1} E_{m-1} - a_{m-1} E_{m-1}^R) f_{m-1} . \quad (4.20)$$

Here $a_m \equiv \exp(-ik_{z_m} d_m/2)$, where d_m is the thickness of the m th layer [45].

At the $m, m - 1$ interface the reflection, R_m , and transmission coefficients, T_m , are defined as

$$R_m = \frac{a_m^{-1} E_m^R}{a_m E_m} , \quad (4.21)$$

and

$$T_m = \frac{a_{m-1}^{-1} E_{m-1}}{a_m E_m} . \quad (4.22)$$

Note that the amplitudes $a_m E_m$, $a_m^{-1} E_m^R$ and $a_{m-1}^{-1} E_{m-1}$ are the values of the incident, reflected and refracted beams, respectively, measured at the interface.

This leads to the recursion relations

$$R_m = \frac{a_{m-1}^4 R_{m-1} + G_m}{a_{m-1}^4 R_{m-1} G_m + 1} , \quad (4.23)$$

and

$$T_m = \frac{1 + R_m}{1 + a_{m-1}^4 R_{m-1}} , \quad (4.24)$$

where

$$G_m = \frac{f_m - f_{m-1}}{f_m + f_{m-1}} . \quad (4.25)$$

Thus if R at one interface is known, then R and T at every interface can be calculated. At the bottom of the substrate there is neither a reflected beam nor a transmitted beam, i.e. $R_0 = 0$ and $T_0 = 0$. In this way the recursion relations can be applied to successive layers from bottom to top to determine R and T at every interface. The reflectivity at the top surface is then given by (using the notation of Figure 4.3)

$$|R_3|^2 = \left| \frac{E_3^R}{E_3} \right|^2 , \quad (4.26)$$

where $|a_3| = 1$ and $f_3 = 0$, where the index $n_3 = 1$.

It is useful to derive a method for calculating the amplitude of the electric field at a given position within the layered structure. From the definitions of the reflection and transmission coefficients at the $m, m-1$ boundary, we have

$$E_{m-1} = T_m a_m a_{m-1} E_m , \quad (4.27)$$

and

$$E_m^R = R_m a_m^2 E_m . \quad (4.28)$$

Referring to Figure 4.3 we may now evaluate the field amplitudes relative to the amplitude, $E_{incoming}$ of the incident wave.

4.3.2 Field Amplitudes in the Crystal

As mentioned earlier the transfer matrix method of Kohn [47] is a straightforward and tidy method of dealing with systems composed of many layers. For SQW structures it is possible to calculate the wave amplitudes (e.g. at the location of the In atoms) based on the principles outlined in the preceding section. For more complicated structures, however, the matrix method is preferred.

In the topmost medium, the n th layer, the “refracted” field amplitude is

$$E_n = E_{incoming} . \quad (4.29)$$

From equation 4.28, the amplitude of the reflected wave is found from the boundary condition (BC) at the $n, n - 1$ interface

$$E_n^R = R_n a_n^2 E_n . \quad (4.30)$$

In medium $n - 1$, the top interface BC gives

$$E_{n-1} = T_n a_n a_{n-1} E_n . \quad (4.31)$$

while the bottom interface BC gives

$$E_{n-1}^R = R_{n-1} a_{n-1}^2 E_{n-1} = (R_{n-1} a_{n-1}^2)(T_n a_n a_{n-1} E_n) . \quad (4.32)$$

For the $n - 2$ layer we similarly find

$$E_{n-2} = T_{n-1} a_{n-1} a_{n-2} E_{n-1} . \quad (4.33)$$

and

$$E_{n-2}^R = R_{n-2} a_{n-2}^2 E_{n-2} = (R_{n-2} a_{n-2}^2)(T_{n-1} a_{n-1} a_{n-2}) E_{n-1} . \quad (4.34)$$

Now, using equation 4.31

$$E_{n-2}^R = (R_{n-2} a_{n-2}^2)(T_{n-1} a_{n-1} a_{n-2})(T_n a_n a_{n-1}) E_n . \quad (4.35)$$

In the GaAs(001)/InAs/GaAs structures studied in this work, the $(n - 2)$ th layer is the quantum well ($m = 1$). The ratio of the total field amplitude in this layer, relative to the incoming field amplitude is then

$$\frac{E_1^{tot}}{E_{incoming}} = (1 + R_1 a_1^2)(a_1)(T_2 a_2^2)(T_3 a_3) , \quad (4.36)$$

which is easily calculated from the reflection and transmission coefficients.

Figure 4.4 shows the results of calculations carried out for layered structures of this type with InAs layers 1 ML thick and GaAs caps of varying thicknesses. The

calculations were performed for an incident photon energy of 200 eV above the In K-edge energy ($E_0=27940$ eV). The structure factors were calculated using the method of Appendix A. It is interesting to note the tremendous increase in the field amplitude at the surface observed at the substrate critical angle. This results from the appearance of an X-Ray standing wave in the crystal as will be discussed. On the linear scale it is not possible to distinguish between the reflectivities for samples with different cap thicknesses. On the logarithmic scale of Figure 4.5 the differences become more apparent.

Figure 4.4: The reflectivity, R , calculated for layered InAs/GaAs structures as described in the text. The electric field intensity at the location of the In atoms is shown for GaAs cap thicknesses of 10 Å, 100 Å, 500 Å and 1000 Å. The largest intensity depicted in the figure corresponds to the value obtained at the topmost surface of the structure.

It is also important to consider the penetration depth of the X-Rays into the

Figure 4.5: The reflectivity, R , calculated for layered InAs/GaAs structures with GaAs cap thicknesses as indicated. The curves were offset by one decade for clarity. Note the very wide angular range of the figure.

crystal as a function of incidence angle. If we define [48] the damping constant, z_0 as

$$z_0 = \frac{\sqrt{2}}{k} [\sqrt{(\theta^2 - 2\delta)^2 + 4\beta^2} - (\theta^2 - 2\delta)]^{-1/2} , \quad (4.37)$$

then it is seen from Figure 4.6 that below the critical angle the energy does not penetrate very far into the crystal. This allows for X-Ray absorption studies of atoms located very near the surface in the so-called “total reflection” geometry. For InAs films buried beneath a GaAs capping layer, however, a slightly deeper incidence angle was required, to ensure that a significant amount of energy propagates through to the location of the In atoms. This will be discussed in more detail in Section 6.7.

It is worth pointing out that for a fixed angle of incidence the reflectivity does not necessarily remain constant during an XAFS scan. As the incident photon energy

is increased through an absorption edge the changing absorption may significantly alter the reflectivity which can then exhibit EXAFS. In the present case, however, the reflectivity is due largely to the GaAs substrate, and the changing photoabsorption from the dilute In atoms has a negligible effect on the reflectivity. A discussion of “reflectivity EXAFS” has been given by Jiang [45].

4.3.3 Total Reflection XSW

In the glancing incidence geometry it is possible to create an XSW field with varying periodicity above a surface [49]. Although this method was not employed in the present study, it is nevertheless worth discussing. As in the Bragg geometry the interference of the two coherent traveling plane waves creates a standing wave with planes of maximum intensity parallel to the surface and with a period

$$D = \frac{\lambda}{2\sin\theta} \quad . \quad (4.38)$$

Figure 4.7 shows the reflectivity and phase of a GaAs crystal as functions of the incidence angle. The phase, α , decreases from π to 0 as θ is increased from 0 to θ_C . From Equation 4.38, the first antinode occurs at infinity for $\theta = 0$. As θ is increased through the range of total reflection, the first antinode moves inwards until it coincides with the crystal surface at $\theta = \theta_C$. As the period decreases throughout this angular range, the remaining antinodes move inwards like a compressing bellows [49]. The compression of the standing wave and the inwards shift, due to the phase change are expressed in terms of the E -field intensity above the surface as

$$I(\theta, z) = |E_0|^2 [1 + R + 2\sqrt{R}\cos(\alpha - 2\pi Qz)] \quad . \quad (4.39)$$

Here $Q = 2\sin\theta/\lambda = 1/D$ is the magnitude of the wavevector transfer. Figure 4.7 also show the θ -dependence of the intensity, I , for $z = 0$ and $z = 2D_C$, where the critical period, $D_C = \lambda/2\theta_C$, is the standing wave period at the critical angle. Standing wave experiments performed in this manner [49] have been used to locate metal atoms up to 200 Å above mirror surfaces with a precision of 2 Å.

Figure 4.6: The reflectivity, R , calculated at 28140 eV for a GaAs crystal and the penetration depth of the X-Rays into the crystal. The dotted line indicates the reflectivity which would be obtained for a non-absorbing crystal where $R = 1$.

Figure 4.7: (a) The reflectivity, R , and phase, α , for a GaAs crystal. (b) The electric field intensity at the crystal surface ($z = 0$) and at twice the critical period ($z = 2D_C$).

The next chapter will summarize previously reported work dealing with InAs layers in GaAs. This will include fundamental issues of strain, epitaxy and optical characterization.

Chapter 5

Review of Literature

In this chapter published reports dealing with the growth and characterization of InAs layers in GaAs will be discussed. As mentioned, the different lattice parameters of InAs and GaAs produce a biaxial strain in the epitaxial structure. In the first section this topic will be discussed, first though a summary of the macroscopic elastic description of the strain accommodation, followed by a review of experiments aimed at direct measurement of the physical properties of such strained layers. In practice the fabrication of very abrupt InAs layers is hindered by In segregation during the GaAs cap layer growth. Previously this process was studied almost exclusively in samples grown by MBE, due largely to the more extensive range of techniques available for *in-situ* studies in UHV. The present work is thus somewhat unique in addressing this phenomenon in MOVPE samples. In the MOVPE environment the predominant *in-situ* characterization technique is RDS which will be discussed in Section 5.3. Finally, optical studies of ultrathin InAs layers in GaAs will be discussed. This will include both theoretical and experimental works aimed at describing the emission properties of these structures.

5.1 Strain in Heteroepitaxy

In the design of semiconductor devices, it is often desirable to use lattice-mismatched layered heterostructures. The SQW structures studied in this work are a particularly

striking example of this, given the bulk lattice constants of GaAs ($a_{GaAs}=5.6532 \text{ \AA}$) and InAs ($a_{InAs}=6.0584 \text{ \AA}$) which differ by $\sim 7\%$. Long ago, the theoretical bases for such heteroepitaxial growth were studied. There are three principal growth modes: layer-by-layer (Frank-van der Merwe); layer-by-layer plus island nucleation (Stranski-Krastanov); and 3-dimensional nucleation (Volmer-Weber) [50]. InAs grows on GaAs (001) in the layer-by-layer mode for approximately 1.5 MLs, after which a transition to the Stranski-Krastanov mode occurs to relieve the strain. InAs “quantum dots” grown by this method are candidates for 0-dimensional quantum confinement and this is an extremely active field of research at this time. The present discussion considers those aspects of strain which are relevant to the heterostructures of interest to this thesis.

5.1.1 Macroscopic Elastic Theory

The theory of materials elasticity is well established [51]. For an epitaxial layer grown coherently on a substrate, i.e. without misfit dislocations, the state of elastic strain may be described by the macroscopic elastic theory (MET) developed by Hornstra and Bartels [52]. They considered strain in III-V compounds for growth planes perpendicular to a symmetric axis (e.g. (001)) as well as for arbitrary growth planes, such as (113).

For an epitaxial layer much thinner than the substrate it may be assumed that there is negligible strain in the substrate. Consider an epilayer in its bulk state, and suppose it is strained in all directions by an amount

$$\epsilon_{\parallel} = \left(\frac{\Delta a}{a_f} \right) , \quad (5.1)$$

where $\Delta a = a_s - a_f$ and f denotes the film layer, s denotes the substrate. If the layer is coherently fitted to the substrate ($a_{\parallel} = a_s$) and the stresses applied to the surface are removed, then the strain parallel to the surface is still $\epsilon_{\parallel} = (a_{\parallel} - a_f)/a_f$, but the perpendicular strain has a different value, $\epsilon_{\perp} = (a_{\perp} - a_f)/a_f$. An additional shear strain will be present if the surface normal is not aligned along a symmetry axis. The components of strain in the two directions are related through the elastic constants

of the epilayer, C_{11} and C_{12} , as

$$\epsilon_{\perp} = -2\left(\frac{C_{12}}{C_{11}}\right)\epsilon_{\parallel} . \quad (5.2)$$

Notice that $\epsilon_{\perp}$ has the opposite sign to $\epsilon_{\parallel}$. The epitaxial layer now has a perpendicular lattice constant different from the substrate, while the in-plane lattice constants are equivalent. An illustration of the strain accommodation is given in Figure 5.1.

Figure 5.1: On the left-hand side the bottom and top images denote a substrate (e.g. GaAs) and an epilayer (e.g. InAs) with a larger lattice constant. The right-hand side illustrates the strain accommodation through a tetragonal distortion of the InAs unit cell. In, Ga and As atoms are indicated by black, white and shaded circles, respectively.

Assuming the validity of the MET we can evaluate the effects of strain on a single ML InAs film buried in GaAs(001) [2]. The elastic constants of InAs and GaAs are given in Table 5.1. From Equations 5.1 and 5.2 the perpendicular lattice constant of the InAs layer is $a_{\perp}=6.4988$ Å. The corresponding In-As plane spacing in the (001)-direction is 1.6247 Å which is stretched by $\sim 15\%$ compared to the value for GaAs. In the bulk InAs lattice with dimension a_{InAs} , the nearest-neighbour bond

Material	C_{11} ($10^{10}Nm^{-2}$)	C_{12} ($10^{10}Nm^{-2}$)
GaAs	11.9	5.38
InAs	8.329	4.526

Table 5.1: Elastic constants of bulk compound semiconductors. From Reference [53].

length is $R_{In-As} = \sqrt{3}a_{InAs}/4 = 2.623$ Å. For the single layer inserted into a GaAs matrix a simple geometric calculation predicts the strained bond length to be slightly compressed, having the value $R'_{In-As} = 2.576$ Å.

For ternary (e.g. $In_xGa_{1-x}As$) or quaternary materials (e.g. $In_xGa_{1-x}As_{1-y}P_y$) the bulk lattice constants are given by Vegard's law. For an $In_xGa_{1-x}As$ film,

$$a_f = xa_{InAs} + (1-x)a_{GaAs} \quad . \quad (5.3)$$

in terms of the bulk lattice constants of the constituents. Similarly, the elastic constants of the film are given by the concentration-weighted elastic constants of InAs and GaAs.

5.1.2 Bond-Lengths in Semiconductor Alloys

In the interpretation of powder diffraction data from ternary alloys the so-called "virtual crystal approximation" (VCA) may be used. For an $In_xGa_{1-x}As$ film, this supposes that the In and Ga atoms occupy the same (virtual crystal) positions and that Vegard's law applies. A pioneering study by Mikkelsen and Boyce [54] used EXAFS to study the In-As and Ga-As bond lengths in a series of powder samples with varying compositions, x . The data showed unequivocally that although the VCA is adequate for diffraction studies, it does not describe the microscopic bond lengths in the alloyed material.

Using K-edge EXAFS for all three elements in the samples, Mikkelsen and Boyce found that the In-As and Ga-As nearest-neighbour bond lengths in an alloy are closer to their respective distances in the pure compounds than to the predictions of the VCA. Their results may be summarized as follows. (i) only small changes in the first neighbour distances were observed; (ii) the widths of nearest-neighbour peaks

in the Fourier Transform of $\chi(k)$ are not broadened by the random solid disorder; and (iii) cation-cation distances peak at a single distance in good agreement with the VCA, while the anion-anion distribution is bimodal, indicating that the anions do not occupy VCA positions. Moreover, the second nearest-neighbours were altered in the alloy as a result of disorder on the cation sublattice. Thus $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys are not virtual crystals at the atomic level, while the cation sublattice does approach a virtual crystal beyond the second-neighbour distance [54].

5.1.3 Structural Studies of InAs SQWs

Many HRXRD studies of thin, buried layers have been reported in the literature. Different approaches have been used to model the data, including the semikinematical approach of Tapfer and Ploog [55, 56], and full dynamical treatments [57]. The main advantage of the semikinematical approach compared with a full dynamical treatment is a decrease in the computation time, at the expense of some precision. Modern personal computers are now sufficiently fast that these approximations are unnecessary. Furthermore, Shufan and Zhenhong have shown that the semikinematical approach is inadequate for structures of any complexity when compared with the full dynamical theory [58].

Using Tapfer's technique, Brandt *et al.* demonstrated the sensitivity of HRXRD to 1 ML InAs films in GaAs with very high resolution [10]. The "flashoff" technique used for preparing the samples will be discussed in some detail in Section 5.2. XRD measurements were obtained using the (004) and (224) GaAs substrate reflections. Recall that a full dynamical diffraction simulation for this type of structure was shown in Figure 3.7.

In these measurements the incident X-Ray wave is scattered by the GaAs substrate and the cap simultaneously at the Bragg angle. The sandwiched InAs layer causes a phase shift between these two waves which produces the observed Pendellösung fringes. The period of these fringes is directly related to the cap layer thickness. This interference effect is influenced by the lattice strain and thickness of the InAs layer, although the layer thickness and composition are highly correlated parameters

making it difficult to distinguish between a single, well-defined InAs ML and two MLs of $\text{In}_{0.50}\text{Ga}_{0.50}\text{As}$, for example. Moreover, the sensitivity of the technique to the InAs layer thickness is reduced as the GaAs cap thickness is decreased. Reference [10] reported an InAs layer thickness of 3.9 ± 0.15 Å, corresponding to 1.2 ± 0.05 ML. This calculation used the MET as described in Section 5.1.1, assuming that the lattice mismatch was accommodated entirely by an elastic tetragonal distortion of the InAs unit cell.

Some confusion arose in the literature due to a subsequent paper by Brandt *et al.* in which high-resolution electron microscopy (HREM) data was supposed to reveal a breakdown of the MET in the limit of ML films [18]. It was reported that although the MET agreed with the results for films 3 ML thick, the HREM images were consistent with a strain of 13% for a single ML. This is nearly twice the value predicted by the MET and suggests In-As bond length conservation for a single InAs ML.

In-As bond-length conservation has been suggested by some theoretical work. An *ab initio* total energy calculation predicted that the In-As bond length for a buried ML in GaAs was only slightly shorter than in the bulk material [59]. Later a valence-force field (VFF) model predicted In-As bond-length conservation similar to Brandt's experimental result [60]

More recently, local density approximation (LDA) [61] and random cluster [62] calculations have predicted strained bond-lengths which agree with the MET, as well as with other experimental results.

Giannini *et al.* reported the first XSW study of a single InAs layer buried in GaAs(001) [1]. Using the "flashoff" technique (Section 5.2) they deposited 1.08 ML of InAs, capped by nominally 275 Å of GaAs, and determined the layer thicknesses with HRXRD using the GaAs (224)-reflection. Their synchrotron XSW measurements at fixed photon energy, using the reflectivity and the In- L_{α} fluorescence, yielded the results $P^H = 1.17 \pm 0.02$, $F^H = 0.58 \pm 0.07$. While the Debye-Waller factor is expected to reduce the measured F^H somewhat, the measured value suggested a high degree of static structural disorder. An alternative interpretation was adopted based on the method described in Section 3.2.2. Given the tendency for In segregation during the cap layer growth (Section 5.2) the measured values of P^H and F^H were explained by

the incorporation of In into “terraces”. Using the MET, a single, highly-strained InAs layer in GaAs would have $P^H = 1.15$. Giannini *et al.* supposed that the effect of In segregation was to distribute the In atoms into three terraces, with 75% of the atoms located at $P_1^H = 1.15$, 20% of the atoms at $P_2^H = 3.45$ and the remaining 5% of the atoms at $P_3^H = 5.75$, relative to the last As-plane of the substrate. Equations 3.54-3.57 verified that the experimental results were consistent with this interpretation. The authors were careful to emphasize that the “terrace nucleation” was different from a graded $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloy [1].

HRXRD studies of single and even subML InAs films buried in GaAs were also reported by Alonso *et al.* [13]. They used symmetrical and asymmetrical reflections to study InAs layers of thickness 0.4-3.2 Å, capped by 1800 Å of GaAs deposited on GaAs (001)- and (311)-oriented substrates, deposited by MBE.

Grazing incidence diffraction (GID) using synchrotron X-Rays was employed by Rose *et al.* to study InAs layers of thickness 0.7-4 ML, buried in GaAs [63]. The films were deposited by MOVPE at 650 °C using TMIIn, TMGa and AsH₃. In the GID measurements the diffracted beam was recorded at an angle nearly perpendicular to the plane of incidence, while the incident beam reflected from each sample at a glancing angle. For exit angles greater than the critical angle, sharp interference fringes were observed in the diffracted intensity. While these interference fringes should, in principle, be related to the layer thicknesses, the GaAs caps were found to have thicknesses only ~84% of their nominal values, while the InAs layers were found to have less than half of their nominal thicknesses. These results could have been verified by comparison with more conventional HRXRD measurements.

Bocchi and Ferrari used HRXRD with several substrate reflections to study the distribution of In atoms in InAs SQWs in GaAs(001) grown by MBE and ALMBE [64]. While the symmetrical (004)-reflection is rather insensitive to the distribution of In atoms, it was shown that the asymmetrical (224)-reflection in the grazing exit geometry could be used to evaluate the distribution of In atoms along the growth direction. It was reported that the measured XRD profiles were consistent with In segregation to a depth of ~6 Å, using Tapfer’s approach [55]. In the article the authors show a

schematic of the segregated In concentration as a function of depth within the crystal. Strangely, this illustration seems to suggest a series of In-containing layers with fractional ML thicknesses. While the physical interpretation of this is unclear, it is also unclear from our dynamical simulations that the experiment could distinguish between single InAs layers and the segregated profiles, as claimed in the article.

To clarify the microscopic structure of InAs layers buried in GaAs, Woicik *et al.* combined XSW and XAFS to determine the displacement of the In atoms from the GaAs (004)-planes, as well as the In-As strained bond lengths [2]. The InAs SQW was grown on GaAs(001) by MBE and capped by 25 Å of GaAs to inhibit oxidation and to provide a bulk termination of the structure. The XSW measurements were performed at beamline X24A at the NSLS using the GaAs (004) back-reflection geometry, and making use of the In- L_α fluorescence signal. They found $P^H = 0.16 \pm 0.02$ and $F^H = 0.73 \pm 0.10$.¹ The corresponding In-As planar distance is equal to 1.64 ± 0.03 Å which agrees very well with the MET prediction of 1.62 Å and the LDA prediction [61] of 1.63 Å.

XAFS measurements performed at the In L_3 -edge were used to further clarify the geometric details [2]. Even with the limited range of k -space available ($4 \rightarrow 7.2$ Å⁻¹) the raw data and least-squares fitting revealed a slight compression in the In-As bond length, with a measured value of $R'_{In-As} = 2.57 \pm 0.02$ Å (compared with the bulk value of $R_{In-As} = 2.623$ Å). These measurements showed conclusively that the MET is applicable down to the ML scale, refuting the anomaly claimed by Brandt *et al.* [18].

An important conclusion from this work is that the principal method for strain accommodation is bond bending, rather than bond stretching [2]. This was established by comparing the energy costs of the two mechanisms. For a central atom in the zincblende lattice surrounded by four nearest-neighbours, the leading terms in the expansion of the total energy with a strain-induced distortion are

$$E\left(\frac{\Delta R}{R}, \theta\right) = -E_0 + 4 \left[\frac{1}{2} k_R \left(\frac{\Delta R}{R} \right)^2 \right] + 3 \left[\frac{1}{2} k_\theta (\Delta \theta)^2 \right] . \quad (5.4)$$

Here k_R and k_θ are the force constants for bond stretching and bending, respectively,

¹Since the coherent position is only determined *modulo*- d_H , the measured value of 0.16 is equivalent to 1.16, to be consistent with the notation used elsewhere in this thesis.

while ΔR and $\Delta\theta$ are the bond stretch and bond bend (Figure 5.2). The second-neighbour distance, d , in the two in-plane directions is given by $d = 2R\sin(\theta/2)$ in terms of the nearest-neighbour bond length, R , and the bond angle, θ . This gives

$$\frac{\Delta d}{R} = 2 \left(\frac{\Delta R}{R} \right) \sin \left(\frac{\theta}{2} \right) + (\Delta\theta) \cos \left(\frac{\theta}{2} \right) . \quad (5.5)$$

Minimizing E subject to this constraint yields the bond-stretching to bond-bending ratio

$$\frac{(\Delta R/R)}{(\Delta\theta)} = \left(\frac{3\sqrt{2}}{2} \right) \left(\frac{k_\theta}{k_R} \right) . \quad (5.6)$$

where the force constants are found in Reference [65]. For InAs this ratio is 0.076, indicating that bond-bending is the dominant mechanism, in agreement with the experimental results [2].

Figure 5.2: The first-neighbour environment of atoms in the zincblende lattice. In this picture the arrows indicate in-plane compressive forces which produce the observed distortions. From Reference [2].

Woicik *et al.* later compared InAs and $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers buried in GaAs(001), even for InAs films beyond the critical thickness [3]. The XSW coherent positions of a 1 ML InAs layer and a 1 ML $\text{In}_{0.48}\text{Ga}_{0.52}\text{As}$ were found to be $P^H = 1.163 \pm 0.02$ and $P^H = 1.053 \pm 0.02$, respectively, with coherent fractions of $F^H = 0.72 \pm 0.1$ and $F^H = 0.53 \pm 0.1$. The lower alloy layer position was attributed to the presence of alternating In and Ga atoms within the plane. The shorter As-Ga-As interplanar distance imposes a compressive force on the longer As-In-As interplanar distance.

For InAs layers of thickness 1, 2, 4 and 8 ML, the trends in the data suggested that the measured coherent positions agreed with the strained layer predictions up to about 1.5 MLs, beyond which the layers relaxed and became disordered. With increasing InAs film thickness F^H approached zero because the layers differ in lattice constant from the GaAs crystal, and are each located at a different distance from the GaAs (004)-planes. This was further illustrated by the In- L_3 XAFS. The 1 ML film exhibited slightly shorter first-neighbour In-As bonds than bulk InAs due to the compressive strain. For the 8 ML film, however, the bond length reverted to its bulk value. It was found that the structural disorder due to the relaxation appeared as a reduction in 2nd and higher shell amplitudes in the XAFS [3].

The InAs 1 ML sample measured with back-reflection XSW in Reference [2] was also measured using XSW at a fixed photon energy of 6 keV by Lee *et al.* [4]. Their value of $P^H = 1.154 \pm 0.01$ agrees very well with the MET prediction, and with Woicik's measurement. However, the coherent fraction was slightly lower, having the value $F^H = 0.43 \pm 0.03$.

Lee *et al.* also measured the displacement between the GaAs substrate and cap using the evanescent wave effect [4]. By positioning the solid-state fluorescence detector at a shallow angle with respect to the crystal surface, and using a pair of slits to select fluorescence emission at a well-defined angle, it was possible to distinguish between signals originating from the top or bottom GaAs layers. When the XSW wavefield passes through the crystal it excites Ga and As fluorescence. A critical angle, θ_C , exists for fluorescent X-Rays travelling out of the crystal just as for incident X-Rays entering the crystal (although the fluorescent X-Rays have lower energy, As- L_{α_1} =1282 eV and θ_C =1.5°). The situation is similar to applying the discussion

of Section 4.3.1 in reverse. So the escape depth of the As L_α fluorescent photons can be adjusted and used to determine the location of As atoms in the substrate and cap, relative to the substrate (004)-planes. For the substrate, the results were $P^H = 1.00 \pm 0.01$ and $F^H = 0.81 \pm 0.01$, obtained at a takeoff angle of 10° . The expected F^H is about 0.9, corresponding to the GaAs Debye-Waller factor [34]. Measurements were then taken at smaller takeoff angles (2° , 3° and 4°). For the cap As atoms the results were $P^H = 0.33 \pm 0.03$ and $F^H = 0.64 \pm 0.12$, corresponding to a 0.47 ± 0.04 Å displacement of the GaAs cap relative to the (004)-substrate planes.

Recently Woicik and collaborators published several experimental [66, 67, 68] and theoretical [62] works aimed at resolving the outstanding issue of bond-length strain in semiconductor-alloy heterostructures.²

In K-edge EXAFS was used to determine the In-As bond lengths in a buried $\text{In}_{0.22}\text{Ga}_{0.78}\text{As}$ film grown coherently on GaAs(001) [66]. The result of $R_{\text{In-As}} = 2.581 \pm 0.004$ Å is essentially identical to the value of 2.582 Å predicted by a simple model based on the MET, assuming strain accommodation through equal distortions of the In-As and Ga-As bonds.

A random cluster calculation was then developed to predict bond lengths using a valence-force field [62]. Bond lengths in sixteen-bond $\text{In}_j\text{Ga}_{1-j}\text{As}$ clusters ($j=0,1,2,3,4$) were calculated separately as a function of composition, x , and then statistically averaged to determine the In-As and Ga-As bond lengths. An illustration of the cluster appears in Figure 5.3. This calculation reproduces Mikkelsen and Boyce's bulk alloy results [54], and enabled the prediction of strained bond lengths in films grown on (001) and (111) surfaces. For the (001)-case, the predicted In-As and Ga-As strained bond lengths are contracted by nearly the same amount for a given composition, x , despite the inequivalent bulk bond lengths.

These predictions were verified by combining the EXAFS results of Reference [66] with diffraction anomalous fine structure (DAFS) measurements obtained at the Ga and As K-edges [67]. The DAFS technique makes use of constant wavevector, $\vec{q}$, measurements, $q = \|\vec{q}\| = (4\pi/\lambda)\sin(\theta)$. Here λ and θ refer to the X-Ray wavelength and

²Reference [68] reports the results of experiments performed in collaboration with SFU, and described in Section 7.9.

Figure 5.3: The sixteen-bond InGaAs cluster used in the model of Reference [62]. The central atom (shaded circle) is As, bonded to j In atoms and $4 - j$ Ga atoms (empty and solid circles), randomly occupying cation sites. The 12 peripheral As atoms of the cluster are bonded to 24 external atoms fixed at their virtual crystal positions.

the incident angle, respectively. For the $\text{In}_{0.22}\text{Ga}_{0.78}\text{As}$ layer buried in $\text{GaAs}(001)$, diffraction measurements reveal a relatively strong layer peak distinct from the substrate (004)-peak. By measuring the intensity of this peak as a function of photon energy it is possible to deduce the local environments of atoms in the layer. This technique has an advantage over conventional XAFS through the elimination of the common-element problem. XAFS at the Ga or As edges is inappropriate for this type of structure because it can not distinguish between signals originating in the strained layer or in the barrier layers. The measurements are possible using DAFS because the strained layer Bragg peak is separated from the substrate peak in reciprocal space [67]. Excellent agreement was found with the random cluster theory [62] predicting equal, compositionally-dependent distortions of the In-As and Ga-As bond lengths.

Two very recent articles by Zheng *et al.* have considered the dynamical diffraction occurring in structures containing 1 ML of InAs buried in $\text{GaAs}(001)$ [69, 70]. The first article describes a full dynamical diffraction treatment. In the second, the theory is applied to experimental measurements of samples grown by MBE, with GaAs caps

of thickness 900 Å. The (004) and (220) reflections were used to determine that the In atoms were displaced by 16% from the (004)-planes, in rough agreement with the MET and XSW results [1]-[4].

5.2 Segregation of Indium in Heteroepitaxy

During the growth of InAs or $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers in GaAs(001), In segregation has been observed by many researchers. While the InAs-on-GaAs surface is rather abrupt, In atoms “float” upwards with the growing surface by exchanging positions with the incoming Ga atoms. For single layers of InAs buried in GaAs, this process occurs during the GaAs cap layer growth. Thus the In distribution is asymmetric with respect to the top and bottom interfaces. In this section the available literature will be reviewed in order to develop a complete picture of the factors influencing segregation and the techniques available for examining this process. At this time there do not appear to have been any published reports examining the segregation process in samples grown by MOVPE.

Among the first detailed segregation studies was the work by Guille *et al.* [8]. During the MBE growth of GaAs/InAs/GaAs structures, *in-situ* surface studies allowed a quantitative description of the segregation process. This involved both Auger Electron Spectroscopy and X-Ray Photoemission Spectroscopy (XPS) measurements of the surface In and Ga signals.

For 1 ML of InAs deposited on GaAs the experimental results [8] showed no cation exchange at the surface. During the cap layer growth, however, significant In segregation was observed. A simple model characterized the segregation by an efficiency coefficient, σ . When the first ML of GaAs is deposited on the InAs ML (layer 1), a fraction σ of the In atoms segregate to the surface, burying the same fraction of the deposited Ga ML. The process continues during the deposition of subsequent GaAs layers, where the composition of the n th layer, $\text{In}_{x_n}\text{Ga}_{1-x_n}\text{As}$, is x_n and

$$x_n = (1 - \sigma)\sigma^{n-1} . \quad (5.7)$$

It was found that the data were best described by this process with a value $\sigma = 0.8 \pm 0.15$.

This effect was originally attributed to the different InAs and GaAs bonding energies (1.41 eV, and 1.59 eV, respectively), in which the more weakly-bonded atom tends towards the surface [8]. Strain and differences in surface reconstruction were also thought to play a role. Suppression of the segregation at higher GaAs growth rates was suggested, but not observed for rates up to 0.5 $\mu\text{m}/\text{min}$. It was also suggested that a high GaAs cap growth temperature could be used to desorb the floating In layer. This was the first mention in the literature of “flashing-off” the segregated In atoms. Later Brandt *et al.* would capitalize on this idea [71].

The same researchers later published an extensive study of segregation involving several III-As heterostructures and ternary alloys [9]. During MBE growth, RHEED, AES, XPS, Ultraviolet Photoemission Spectroscopy (UPS), and Electron Energy Loss Spectroscopy (EELS) were used to evaluate the extent of segregation, and to establish the tendencies for segregation ($\text{In} \geq \text{Ga} \geq \text{Al}$). Some samples were also studied *ex-situ* using Rutherford Backscattering (RBS). For the GaAs/InAs/GaAs system, the In segregation efficiency was again found to be near $\sigma = 0.8$, independent of T_g from 420 °C to 560 °C, and independent of the GaAs cap growth rate.

It was noted [9] that thermodynamically, segregation at a growing surface occurs as the system attempts to balance the chemical potentials of the segregating atom in the bulk, μ_b , and at the surface, μ_s . This is the same mechanism driving the epitaxial process itself (Section 2.4), where the balance occurs between the chemical potentials in the (supersaturated) vapour, and in the growing solid. If the movement of a given species from the bulk to the surface yields a positive energy, E_s , then the chemical potentials in these regions are not equal for a homogeneous concentration. Instead, the surface concentration, x_s , is higher than the concentration, x_b , in the bulk.

To model the thermodynamics of the process, the balance of chemical potentials was described by McLean’s equation [72]

$$\ln\left(\frac{x_s}{1-x_s}\right) + \frac{E_s}{kT_g} = \ln\left(\frac{x_b}{1-x_b}\right) . \quad (5.8)$$

To account for the strain, this equation was rewritten to include the elastic energy as

$$\ln\left(\frac{x_s}{1-x_s}\right) + \frac{E_s}{kT_g} + \frac{C'a^3}{4kT_g}\left(\frac{\delta a}{a}\right)^2\left(1 + \frac{\delta a}{a}(x_s + x_b)(x_s - x_b)\right) = \ln\left(\frac{x_b}{1-x_b}\right) \quad , \quad (5.9)$$

where $C = (C_{11}^{\text{InAs}} + C_{11}^{\text{GaAs}})/2$ is the mean elastic constant, a the GaAs lattice parameter, and $\delta a/a$ the lattice mismatch between InAs and GaAs. The scaling elastic factor, $C'a\delta a^2/4kT_g$ has a value of approximately 2 for the In-Ga-As system at 527 °C, where $C \approx 0.6 \text{ eV/\AA}^3$.

For high bulk concentrations and the usual low growth temperatures, the chemical potential in the bulk phase and the segregation energy are too high to be counteracted by disorder or elastic strains, and the surface concentration of the segregating species, x_s , is near unity. It was remarked that flashoff is the only way to reduce the surface concentration under these conditions [9].

To explain the observed segregation order ($E_{\text{In}} > E_{\text{Ga}} \geq E_{\text{Al}}$) it was noted that the bulk bonding energies (InAs 1.41 eV, GaAs 1.59 eV, AlAs 1.98 eV) are consistent with the principle of the more weakly-bonded species segregating to the surface [9]. This arrangement did not explain the segregation order for antimonides, however (bonding energies: GaSb 1.50 eV, AlSb 1.79 eV). The bond length orders explain the results for both As and Sb compounds, where $R_{\text{In-As}} (2.62 \text{ \AA}) > R_{\text{Ga-As}} (2.45 \text{ \AA}) \approx R_{\text{Al-As}} (2.45 \text{ \AA})$; and $R_{\text{Ga-Sb}} (2.64 \text{ \AA}) > R_{\text{Al-Sb}} (2.66 \text{ \AA})$.

Predictions of the segregating species were not [9] expected to be straightforward, and it was noted that the order could be reversed for different crystal orientations. Indeed, He *et al.* recently observed Ga segregation for InAs growth on GaAs(110) using soft XPS [73]. Other factors such as the surface reconstruction or relaxation, not taken into account by the modified McLean equation, were also expected to be involved in the process.

Since the cation exchange reactions are rapid with respect to the growth, segregation was not supposed to be kinetically limited under usual growth conditions [9]. Reducing segregation by manipulation of the kinetics was suggested, and could be effected by decreasing the migration rates of the atoms at the interface, the number of reaction sites, and/or the rate of reaction at these sites.

According to the thermodynamic model, decreasing T_g favours segregation but

decreases the surface migration [9]. Thus alternating flux epitaxies (ALE or its MBE counterpart, migration-enhanced epitaxy (MEE)) seem to be unsuitable for producing abrupt interfaces because of the high cation surface mobilities, unimpeded by excess anion flux. It was suggested that growth of the GaAs overlayer using a low-surface-mobility technique would result in sharper interfaces.

Observations of In segregation have been made using RHEED oscillations [74] during chemical beam epitaxy (CBE) of InGaAs, as well as in MEE [75]. In the latter, characteristic oscillations in the RHEED intensity were observed during the alternating Ga and As fluxes of the MEE cycle. When a single In pulse was substituted for a Ga pulse, a marked decrease in the RHEED amplitude occurred for growth temperatures of 400, 500 and 560 °C. When the GaAs capping cycles were initiated the surface recovered to its original state for growth at 400 and 560 °C, but not at 500 °C. Secondary ion mass spectroscopy (SIMS) suggested that the incorporated In was less than expected for the 560 °C sample, indicating In evaporation. The In SIMS profile was found to be asymmetric for the 500 °C sample, but symmetric for the others. This suggests that the In segregation increases with increasing T_g , until higher temperatures at which the desorption removes the segregating atoms. The segregation was attributed to the difference in InAs and GaAs bonding energies, although previous work suggested otherwise [9].

The “flashoff” technique mentioned earlier was realized by Brandt *et al* [10], who studied the structural and optical properties of their films using HRXRD, double-crystal X-Ray reflection topography, HREM, PL and PL excitation (PLE). Buried layers of InAs in GaAs(001) were deposited by MBE using the following sequence. A 1 μm GaAs buffer was deposited at 540 °C, followed by the InAs layer growth at 420 °C. A few ML of GaAs were then deposited at 420 °C, after which a thicker GaAs cap was grown at 540 °C. The hypothesis was that any segregated In would be contained within (at worst) the first few cap MLs, and that heating to 540 °C desorbs the excess In. The term “flashoff” was coined later [71].

HRXRD data were interpreted using a semi-kinematical description [55] assuming coherency of the InAs layer with the substrate, and strain accommodation by an elastic deformation of the InAs unit cell [10]. The simulations suggested an InAs

layer thickness of 1.2 ML and X-Ray reflection topographs confirmed the absence of structural dislocations. The InAs-on-GaAs growth rate was only 64% of the bulk InAs growth rate because the heteroepitaxial strain acts as a kinetic barrier to the incorporation of In atoms in the crystal. This indicates the complexity of the growth process at the level required for characterizing these ultrathin films.

A review by Moison *et al.* [76] including results of surface studies, HREM, RBS, PL and Raman scattering drew the same conclusions as the earlier work. Using the thermodynamic prediction of reduced segregation at elevated temperatures, it was noted that the required temperatures are too high ($> 1000\text{ }^{\circ}\text{C}$) to be suitable. Reducing segregation by slowing down the kinetics was suggested, though it was thought that GaAs growth rates could not be increased enough to bury the In atoms before their migration to equilibrium positions on the surface.

Brandt *et al.* discussed the details of the “flashoff” technique in a later work [71]. Due to the apparent independence of segregation on growth parameters (temperature and material fluxes) for typical MBE procedures, the flashoff sequence was suggested as a means of combatting the kinetic and thermodynamic barriers to the formation of abrupt interfaces. Their InAs layer was deposited in increments of 0.6 ML, annealing the surface under As_4 for 120 s at $420\text{ }^{\circ}\text{C}$ after each deposition. The capping scheme was similar to that described earlier [10] where the thickness of the low T_g cap is an essential parameter. Structures grown in this way were evaluated by RHEED *in-situ*, HRXRD and HREM.

RHEED patterns obtained during the deposition of the InAs layer and GaAs cap were used [71] to study the evolution of the surface reconstructions. When the temperature was lowered for InAs growth, the GaAs (2×4) reconstruction changed to the $c(4\times 4)$, due to excess As_4 adsorption. After the first incremental InAs deposition a (2×3) pattern emerged, corresponding to As_4 -stable conditions. Since the impinging fluxes favoured In-rich conditions, the As termination was attributed not to the impinging As_4 flux, but to the excess As already present on the GaAs surface. After the second increment the reconstruction streaks disappeared, but developed again during the growth interruption. Thus the growth interruptions apparently played an important role in allowing the dynamic recovery toward an equilibrium surface state. When

the GaAs cap growth was initiated a (1×1) pattern was observed, due to the floating In layer. Raising the temperature produced a well-defined $(2 \times 4)_r$ reconstruction, apparently related to the flashoff of the floating In surface layer. The In incorporation in flashed-off samples was estimated to be 40% less In than in films without the flashoff, while the amount of segregated In was found to be insensitive to the growth conditions [71]. An exception appeared in samples grown by MEE with segregation rates of up to 90%.

Structural quality in the flashoff films was evaluated by HRXRD [71]. Buried InAs SQWs of thickness 3.6 ML and SLs with 0.8 ML of InAs were produced with low T_g for the initial 3 MLs of the GaAs cap layer growth. Symmetric and asymmetric HRXRD data were modelled using Tapfer's approach and assuming pseudomorphism with the GaAs substrate. The agreement between the data and the theoretical models up to the 11th-order superlattice satellites was attributed to the InAs layer perfection. For the InAs SQW it was found that the InAs thickness remaining after the flashoff was only 2.4 ML, indicating that 1/3 of the amount deposited was desorbed in the flashoff. HREM images of the heterointerfaces were presented as evidence of the atomic scale interfacial abruptness, and of the structural equivalence of the top and bottom interfaces [71].

Gérard *et al.* used an optical approach to study the segregation effect in InAs layers deposited by MBE at 540 °C within GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ quantum wells [77]. The idea was that the PL spectra would be affected by the position of the InAs layer, either close to the bottom or the top GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ interface. Segregation would spread the In distribution towards the top interface, leading to emission energies different from the QW with the InAs deposited closer to the bottom interface. Observed differences in the emission energies for QWs of this type were interpreted using the model of Equation 5.9 yielding a segregation energy, E_s , in the range of 0.15-0.20 eV, in agreement with Reference [9].

Hansen *et al.* studied the bulk and near-surface composition of $\text{In}_x\text{Ga}_{1-x}\text{As}$ epilayers of 0.5-1.0 μm thicknesses (fully relaxed), grown on GaAs(001) by CBE at temperatures from 470→600 °C, and with different TEIn flow rates [78]. *In-situ*,

the bulk compositions were determined from the change in RHEED oscillation periods. The bulk In content was determined by *ex-situ* XRD, while XPS was used to evaluate the near-surface composition profiles. Comparing the x -values deduced from XRD and from Fourier analysis of the RHEED oscillations, it was found that RHEED consistently underestimates the mole fraction. The data obtained by both methods were highly correlated at 470 °C, but not for higher temperatures. This discrepancy was associated with competitive incorporation of TEGa and TEIn. At the high temperatures surface desorption was thought to play a role in the surface kinetics. The underestimation of the In fraction could be explained by the fact that the RHEED transients were measured in the early, pseudomorphic stages of growth, while the XRD data were obtained following the relaxation of the layer. XPS analysis showed little segregation occurring at 470 °C. At higher temperatures, analysis of the Ga 3p and In 3p peaks showed Ga surface depletion accompanied by an In enrichment extending 50-75 Å into the samples.

Using flow-rate modulation epitaxy (FME), in which an alternating supply of organometallic alkyls and arsine were transported to the reactor, Sato *et al.* prepared pairs of InAs SQWs in GaAs [79]. FME differs from ALE in that small amounts of the group V source accompany the group III flow to the reactor. A theoretical model was derived to include segregation effects in the prediction of PL emission energies. For FME samples with different GaAs spacings between the two InAs layers, the PL energies were well described without In segregation. It was suggested [79] that dangling bonds of the surface As atoms were terminated by H atoms which prevented the In/Ga exchange. In contrast, when this model was applied to the experimental results of Gérard *et al.* [77] for MBE films, a segregation efficiency of 90% was found.

The influence of In segregation on quantized energy levels in InGaAs/GaAs QWs was studied by Muraki *et al.* using SIMS and PL [80]. Growth condition effects were studied by preparing a series of samples with constant well widths and different growth temperatures, or constant T_g and different well widths. It was found that the $1/e$ -decay length of the In SIMS signal increased from 8 Å to 29 Å when T_g was increased from 370 to 520 °C. Although the segregation was reduced for growth below 420 °C, the PL intensities were lower due to the poor crystalline quality of the material. The

best PL emission was obtained in the samples grown at 520 °C. A model for the PL emission energies showed that including the segregation-related compositional grading was necessary to reproduce the experimental transition energies. The segregation was thought to be kinetically limited at the lowest growth temperatures, increasing with increasing temperature, and reduced above 570 °C due to In desorption.

SIMS was also used by Kawai *et al.* to study the spread of the In distribution in MBE samples grown from 400→530 °C [81]. The samples were prepared by growing a GaAs buffer layer at 580 °C and then allowing the substrate to equilibrate at the desired T_g . A single InAs ML was then deposited, followed by 2000 Å of GaAs at the same temperature. It was found that the In spreading width observed with SIMS was present even at 400 °C and increased with increasing T_g . Thicker InAs layers were also prepared, and suggested that the segregation was markedly increased when dislocations were generated near the interface.

Increasing segregation with increasing T_g was also observed in RHEED and UPS studies of InGaAs/GaAs samples prepared by MBE between 490 and 585 °C [82, 83]. The segregation was apparently also reduced at higher V/III ratios. PL spectra for these samples were modelled using a stepwise approximation to the segregated In profiles yielding good agreement with the experimental emission energies. This involved the use of Equation 5.8 with a segregation energy of $E_s=0.22$ eV. The temperature dependence of this equation was not discussed. Throughout the growth sequence the following evolution of the RHEED pattern was observed [82]: (2×4) during the GaAs buffer layer, (1×1) during the InGaAs, (1×1) during the beginning of the GaAs overlayer, and (2×4) after ~12 ML. It was noted that enhanced segregation was associated with a delayed recovery to the (2×4)-reconstruction. When the samples were cooled under As pressure, the (1×1) and (2×4) patterns were transformed into (1×3) and c(4×4), respectively.

The conflicting requirements for minimizing the effects of interface roughness and surface segregation were pointed out by Bosacchi *et al.* [84]. While segregation could be reduced at lower T_g , the roughness is minimized at higher temperatures which, unfortunately, enhance the cation migration at the growth front. Using conventional MBE and atomic layer MBE (ALMBE) to produce a series of InGaAs MQWs and

InAs SQWs in GaAs, the segregation was studied using PL. SQW samples were prepared by growing thick ($0.9\ \mu\text{m}$) GaAs buffer layers at $600\ ^\circ\text{C}$ and then decreasing the temperature. Thinner GaAs barriers ($0.1\ \mu\text{m}$) were deposited at different temperatures between 300 and $495\ ^\circ\text{C}$, followed by the growth of the InAs MLs at the same temperature and a growth rate of $0.06\ \mu\text{m/hr}$. For the MBE samples, the temperatures were linearly ramped to $600\ ^\circ\text{C}$ during the growth of the GaAs cap layers. ALMBE caps were deposited at the same temperature as the InAs layers and with growth rates of $1.3\ \mu\text{m/hr}$.

PL spectra obtained at $10\ \text{K}$ revealed redshifts of the emission energies with decreasing T_g [84] and saturation of the transition energies at minima corresponding to minima of In surface segregation. ALMBE samples exhibited enhanced segregation effects, evidenced by the higher transition energies compared with the MBE samples. This was attributed to the greater exchange reaction rates during the ALMBE group-III sub-cycles. In the absence of an accompanying As flux, the Ga can more easily exchange positions with previously adsorbed In atoms. Saturation of the PL energies was observed at growth temperatures of 260 and $340\ ^\circ\text{C}$ for the ALMBE and MBE samples, respectively. The PL energy curves were found to be concave up with respect to T_g .

The temperature dependence of the thermodynamic model (Equations 5.8 or 5.9) was considered by Dehaese *et al.* [85]. An *increase* in segregation with *decreasing* growth temperature is predicted because of the term $\exp(E_s/kT_g)$. As the preceding discussion clearly shows, this is not consistent with the available experimental data. A kinetic model was developed to address this issue for InGaAs growth following work for dopant incorporation and segregation in MBE growth [86, 87, 88]. The following discussion will adopt the notation of Harris *et al.* who studied Sn incorporation and segregation in MBE-grown GaAs. The case of In segregation in GaAs is analogous.

A schematic representation of the In/Ga exchange process is reproduced in Figure 5.4, where E is the free energy of the system. The distance between the energy minima is roughly equal to the ML thickness and E_s is the segregation energy of the equilibrium model.

Suppose that the initial surface coverage of In is $N_0\ \text{atoms/cm}^{-2}$, and that the

Figure 5.4: Schematic representation of the energy of an In atom as a function of depth within a GaAs film. Each minimum corresponds to a cation plane, with spacing $a_{GaAs}/2$ in the (001)-direction. The solid line represents the initial situation and the dashed line shows the situation after the deposition of an additional GaAs ML. From Reference [87].

InAs layer has been capped by a single GaAs ML. In Figure 5.4, E_1 is the energy barrier for segregation and E_2 is the barrier for the reverse process. The transition probabilities for the two processes are P_1 and P_2 , respectively. After 1 capping ML the original In surface becomes layer $(s-1)$, while s is the new surface. The time evolution of the number of atoms per unit area in layer $s-1$, N_{s-1} , is

$$\frac{dN_{s-1}}{dt} = -P_1 N_{s-1} + P_2 N_s = P_1 (\phi N_s - N_{s-1}) \quad , \quad (5.10)$$

where $\phi = P_2/P_1$. Since $N_s + N_{s-1} = N_0$, this becomes

$$\frac{dN_{s-1}}{dt} = P_1 [\phi N_0 - (1 + \phi) N_{s-1}] \quad , \quad (5.11)$$

which has solution

$$N_{s-1} = \frac{N_0}{(1 + \phi)} (\phi + \exp[-P_1(1 + \phi)t]) \quad , \quad (5.12)$$

making use of the BC $N_{s-1} = N_0$ at $t = 0$ (the In atoms are completely buried for a brief instant).

The equilibrium situation may be considered in the limit as $t \rightarrow \infty$ [87]. Then $N_{s-1} = N_0\phi/(1 + \phi)$ and $N_s = N_0/(1 + \phi)$. In thermal equilibrium,

$$\frac{N_{s-1}}{N_s} = \phi \quad (t \rightarrow \infty) \quad . \quad (5.13)$$

The quantity ϕ is related to the free energy difference which drives the segregation

$$\phi = A \exp\left(\frac{-E_s}{kT_g}\right) \quad , \quad (5.14)$$

where A contains the vibrational frequency and other factors related to the hopping probabilities [87].

Consider GaAs cap growth at a rate 1 ML per τ seconds. If the next GaAs ML growth starts before the In atoms reach their equilibrium distribution, then there is a kinetic limitation to the segregation process. This will dominate when the segregation is slow compared with the ML deposition rate: low T_g or high growth rates. In contrast, at high temperatures or low growth rates the kinetic effects will be small and the incorporation process will tend towards the equilibrium segregation limit. Harris *et al.* derived an equation for the incorporation constant, k_z , which is valid over all temperature and growth rate regimes [87].

If 1 ML of GaAs, thickness $a_{GaAs}/2$, is deposited in a time τ , then

$$N_s(\tau) = \frac{N_0}{(1 + \phi)} (1 - \exp[-P_1(1 + \phi)\tau]) = N_0\sigma \quad , \quad (5.15)$$

where σ is the segregation efficiency as in equation 5.7. After depositing q MLs, the In coverage of the original surface layer, $(s - q)$, will be $N_0(1 - \sigma)$. For subsequent layers

$$\begin{aligned} (s - q + 1) &\rightarrow N_0\sigma(1 - \sigma) \\ (s - q + 2) &\rightarrow N_0\sigma^2(1 - \sigma) \\ (s - 1) &\rightarrow N_0\sigma^{(q-1)}(1 - \sigma) \\ s &\rightarrow N_0\sigma^q \end{aligned}$$

This is an exponentially decaying distribution up to layer $s - 1$, equivalent to the distribution described by equation 5.7. If the In distribution along the z -growth direction has the form [87]

$$n(z) = n_0 \exp(-k_z z) \quad . \quad (5.16)$$

then we note that since

$$N_{s-1} = N_{s-q} \exp[(q-1) \ln \sigma] \quad , \quad (5.17)$$

and $z = (q-1)a_{GaAs}/2$, the decay parameter has the form

$$k_z = \frac{-1}{(q-1)a_{GaAs}/2} \ln(N_{s-1}/N_{s-q}) = \frac{-1}{a_{GaAs}/2} \ln \sigma \quad . \quad (5.18)$$

Using Equation 5.15,

$$\left(\frac{a_{GaAs}}{2}\right) k_z = \ln(1 + \phi) - \ln[1 - \exp[-P_1(1 + \phi)\tau]] \quad . \quad (5.19)$$

For high T_g and relatively slow growth rates (τ large) the first term on the right dominates and

$$\left(\frac{a_{GaAs}}{2}\right) k_z \approx \phi \equiv \exp(-E_s/kT_g) \quad . \quad (5.20)$$

For low T_g and fast growth rates it is assumed that the transition from s to $s - 1$ proceeds according to

$$P_1 = P_0 \exp(-E_1/kT_g) \quad . \quad (5.21)$$

corresponding to a barrier of height E_1 . This gives

$$\ln(k_z a_{GaAs}/2) = -P_0 \tau \exp(-E_1/kT_g) \quad . \quad (5.22)$$

This model was shown to describe MBE results for Sn segregation both in the high- T_g regime, and at low temperatures where kinetic barriers prevent the equilibrium surface concentration from being achieved [87]. However, the model neglects any dependence of the segregation on the As flux or on the incoming V/III ratio. It was pointed out [87] that the important parameters may not be the incident fluxes so much as the surface concentrations of the various species, which are difficult to measure. The segregation is likely to be influenced by adatom populations in either chemisorbed or precursor states which may not be directly controlled.

In the formulation of Reference [85] it was found that the kinetic limitation of segregation for InGaAs growth occurs below 400 °C, and for growth rates in excess of about 1 ML/s.

It is interesting to note that the model of Reference [87] shows two distinct regimes. Williams *et al.* [89] observed this type of behaviour using *in-situ* UPS and RHEED during the growth of GaAs/InGaAs/GaAs(001) structures by MBE. Following the deposition of 5-10 ML of $\text{In}_{0.30}\text{Ga}_{0.70}\text{As}$ a rapid increase in the In surface concentration was observed with increasing temperature during the GaAs cap layer growth. An Arrhenius plot showed that the In segregation consisted of two components. Below 500 °C a “fast” component was observed with an activation energy of 0.18 eV. Above 500 °C a “slow” component with activation energy of 2.49 eV was observed, accompanied by a change in the surface reconstruction. The InGaAs surfaces displayed (1×3) reconstructions, while the GaAs cap surfaces showed (2×2) patterns at lower temperatures. At higher temperatures, the (2×2) surfaces did not appear, suggesting that a significant amount of In remained on the surface [89]. It was noted that the slow component could be due to the generation of misfit dislocations.

Arès *et al* used RDS to study the evolution of surface anisotropies during the ALE growth of GaAs/InAs/GaAs(001) structures, as well as the reverse “antiwell” (InAs/GaAs/InAs(001)) structures [90]. During a typical ALE cycle for the growth of 1 ML of material the 2.56 eV RDS transient exhibits a characteristic pattern. During the growth of several MLs the signal is periodic and highly reproducible from cycle-to-cycle. When a single In pulse was substituted for a Ga pulse in the sequence, the RDS signal became strongly positive, and the shape of the individual cycles was strongly modified during the growth of the following GaAs cap layers. The recovery of the unperturbed GaAs cycle signal required more than 20 ML of growth, indicating a high degree of segregation.

In contrast, during the antiwell growth, the InAs cycle signal was recovered in less than 2 ML [90]. This complementary experiment was particularly useful in that it demonstrated that (i) the slow recovery of the GaAs signal in the QW growth was not the result of reactor memory effects, (ii) the slow recovery was not due to a buried anisotropy associated with the heteroepitaxy, and (iii) as expected, In has a greater

tendency for segregation on the (001) surface.

In the segregation models previously discussed the segregation energy, E_s , cannot be evaluated *a priori* from the growth characteristics. A Monte Carlo simulation for InGaAs growth on GaAs was developed by Grandjean *et al.* which accounts for the binding energies of the constituents, the epitaxial strain and the growth parameters [91]. It was found that the experimental PL emission energies were well-described by the simulation results with the relevant growth parameters.

In the simulations the “hopping rate”, h , was defined as $h = h_0 \exp(-E_d/kT_g)$ (c.f. Equation 5.21), where $h_0 = kT_g/\pi\hbar$ is the adatom vibration frequency ($h_0 = 3.2 \times 10^{13} \text{s}^{-1}$ at 500 °C). Here E_d is the energy barrier to surface diffusion which consists of a substrate contribution, E ; a contribution due to the number of nearest neighbours in the (110) and $(\bar{1}\bar{1}0)$ directions, $pE_{(110)} + qE_{(\bar{1}\bar{1}0)}$; and an elastic energy contribution, E_e which opposes the other factors. The quantities $E_{(110)}$ and $E_{(\bar{1}\bar{1}0)}$ are the axis-dependent bonding energies with the nearest neighbours ($p, q \sim 0.2$). A ratio of $E_{(\bar{1}\bar{1}0)}/E_{(110)} \sim 6$ was used in the calculation [91]. The elastic term was calculated from $E_e = (1 - \alpha_n)E_e^{(n=4)}$, where $E_e^{(n=4)} = 134 \text{ meV}$ is the elastic energy for a tetragonal distortion with 4 nearest neighbours and the coefficient α_n accounts for free surfaces with dangling bonds.

The model developed in this way was found to provide good agreement with experimental PL energies, and showed the importance of including the elastic strain [91]. It was demonstrated that increasing the growth rate or decreasing T_g could be used to kinetically limit the segregation process.

Segregation effects on the optical properties of MBE-grown QWs were later studied by the same researchers in collaboration with Disseix *et al.* [92]. The kinetic approach of Reference [85] was used to analyze the thermally detected optical absorption (TDOA) data obtained for InGaAs/GaAs(001) structures prepared under various conditions of temperature and growth rate. In the TDOA technique the heating of the sample caused by phonon emission due to nonradiative deexcitation, which occurs after optical absorption, is detected by a thermometer maintained with the sample at low temperature (0.35 K was obtained in a ^3He refrigerator).

In the data analysis, the kinetic model was used to describe the In segregation [92].

These results were incorporated into an effective-mass model for the confinement energies in the QWs. Experimental data indicated that the effect of segregation was to increase the transition energies, and that a kinetic limitation is effected at low T_g . Fitting the data yielded a segregation energy of $E_s = 0.13 \pm 0.01$ eV. It was noted that decreasing T_g by 50 °C at a fixed growth rate of 0.5 ML/s had more of an effect on the segregation than an increase in the growth rate from 0.5 ML/s to 1.3 ML/s at 500 °C.

Yamaguchi *et al.* also employed the kinetic segregation model to describe data obtained by SIMS and PL for InGaAs/GaAs(001) samples prepared under various MBE growth conditions [93]. Growth temperatures of between 430 and 500 °C were used, with growth rates between 0.2 and 1.6 ML/s, and V/III ratios between 8 and 27. Increasing segregation was observed with increasing T_g , which saturated at about 550 °C. This was attributed to the convergence of the kinetic and equilibrium descriptions of the segregation process at higher temperatures. PL results indicated an increase in segregation with decreasing cap growth rate as seen in the PL blueshifts. Although the As flux was not included in the kinetic model, it was found experimentally that the segregation was enhanced by low As pressures which produced In-stabilized surfaces. The segregation energy was found to be about 0.10 eV for growth under As-stabilized conditions.

5.3 Reflectance Difference Spectroscopy

For characterization of growing surfaces during MOVPE, the optical techniques of RDS and ellipsometry have found widespread use, since electron-beam techniques such as RHEED are prohibited in non-UHV environments [94]. RDS measures the difference between the normal-incidence reflectances, $\hat{r}_{\bar{1}10}$ and $\hat{r}_{110}$, for light polarized along the $[\bar{1}10]$ and $[110]$ principal axes of the (001) surface [95]. This quantity is determined experimentally as a function of photon energy and growth conditions. Bulk contributions dominating each of the reflectances are nearly identical and cancel in subtraction, leaving a difference related to the surface anisotropy. This surface-sensitivity is the major strength of RDS.

RDS measures the optical anisotropy of III-V crystals through the quantity

$$\frac{\Delta \tilde{r}}{\tilde{r}} = \frac{2(\tilde{r}_{\bar{1}10} - \tilde{r}_{110})}{(\tilde{r}_{\bar{1}10} + \tilde{r}_{110})} = \frac{\Delta r}{r} + i\Delta\theta \quad . \quad (5.23)$$

An example of a RDS spectrum obtained in the SFU system is shown in Figure 5.5. The data presented in this thesis show the real part of the RDS,

$$\frac{\Delta r}{r} = 2R\epsilon \left[\frac{\tilde{r}_{\bar{1}10} - \tilde{r}_{110}}{\tilde{r}_{\bar{1}10} + \tilde{r}_{110}} \right] \quad , \quad (5.24)$$

which is primarily related to the imaginary part of the dielectric function [96].

Figure 5.5: An RDS spectrum of the GaAs(001) d(4×4) reconstruction (disordered c(4×4)). The spectrum was obtained at 550 °C and 50 Torr under TBAs.

Early on, a “database” was established for GaAs surfaces by associating RDS spectra with known surface reconstructions determined by RHEED [97]. This has allowed subsequent work to refer directly to these data. Figure 5.6 shows two common reconstructions of the GaAs(001) surface. The oscillating electric field of the linearly-polarized light causes transitions related to dimers oriented along the principal axes of the crystal. The major features of the RDS spectra may be related to these electronic

transitions. For transient RDS spectroscopy on GaAs(001) it is often useful to monitor the RDS signal near 2.5 eV, which is associated with As dimers on the surface and is particularly sensitive to the nature of the reconstruction. In Figure 5.5 the minimum at 2.5 eV is due to As dimers oriented along $[110]$. The $d(4 \times 4)$ reconstruction is formed by adding excess As to $c(4 \times 4)$ and is distinguishable from the $c(4 \times 4)$ by the RDS peak at 4.0 eV [97].

Figure 5.6: Models of the a) $c(4 \times 4)$ and b) (2×4) reconstructions of GaAs(001). Larger circles indicate atoms closer to the surface. From Reference [98].

Kamiya *et al.* studied the GaAs(001) surface extensively using RDS and identified reconstructions in atmospheric pressure environments (H_2 , He and N_2) similar to those observed in UHV [97, 98, 99]. The temperature dependence of the RDS spectra was similarly explored. Additionally, the RDS and RHEED data obtained under dynamic surface conditions clearly showed a correspondence between the two

techniques, establishing RDS as a suitable tool for controlling epitaxial growth [95].

In the MOVPE environment, Aspnes *et al.* studied processes occurring during ALE growth using transient spectroscopy at 2.5 eV [100]. A novel technique was later developed to allow a complete real-time investigation of the surface evolution during ALE growth [101]. The technique exploits the reproducibility of individual ALE cycles to obtain time-resolved data with very high temporal resolution. Multitransient spectroscopy was performed by acquiring a set of transient spectra, each obtained at a fixed energy from 1.5 to 5.5 eV in steps of 0.5 eV, with each transient synchronized to the same instant of the exposure cycle. The data were then reorganized to form a series of energy spectra, each corresponding to a specific instant in the ALE cycle. This technique was applied in this thesis to allow the observation of the surface anisotropy development during SQW growth sequences at a range of growth temperatures (Section 7.6.1).

Further evidence of the sensitivity of RDS to surface reconstructions was obtained in simultaneous measurements using RDS and grazing incidence X-Ray scattering (GIXS) performed at SSRL [102, 103]. MOVPE growth was performed in a specially-designed vertical reactor [104] which allows the *in-situ* GIXS measurements. The RDS spectrum of the GaAs(001) under TBAs was found to be virtually identical to Figure 5.5, which was obtained in a similar reactor under similar conditions. GIXS measurements made along the [110] and $[\bar{1}10]$ azimuths revealed distinct peaks associated with the $c(4\times4)$. A Ga-rich (4×6) reconstruction was observed upon exposing the sample to TEGa. By varying the measurement conditions slightly it was possible to produce the (4×6) , (2×4) and (4×2) reconstructions [102, 103].

Transient RDS signals monitored during GaAs growth were found to be highly correlated with crystal truncation rod (CTR) X-Ray intensity oscillations arising from the nucleation, growth and coalescence of islands during layer-by-layer growth [102, 103]. Similar to the RHEED case, the cyclic roughening and smoothing of the surface causes the CTR intensity to decrease and then to recover.

For technologically relevant III-V heterostructures RDS has been employed in both time-resolved measurements and in studies of alloy compounds and SL structures [105, 106]. Koch *et al.* studied heteroepitaxy in several materials combinations:

InGaAs, $\text{In}_{0.75}\text{Ga}_{0.25}\text{As}_{0.5}\text{P}_{0.5}$, $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}_{0.9}\text{P}_{0.1}$ and AlInAs on InP(001); and InGaP on GaAs(001). When heterojunctions were grown by MOVPE, the RDS signals changed abruptly at the onset of growth of a new material. Each materials combination exhibited a characteristic “signature” which was quite reproducible and dependent upon the wavelength of illumination. The signal typically rises to a maximum and then exhibits damped oscillatory behaviour. This behaviour was attributed to interference of the light at the buried interface: the growing layer acts as a Fabry-Pérot cavity. A model for the reflection and transmission of light at the surface and the buried interface was used to model the oscillations which occur over a time scale of several minutes, from which the layer thicknesses were determined [105].

Zorn *et al.* performed RDS studies during the growth of ternary alloys on GaAs(001) with alloying on either the group III ($\text{In}_x\text{Ga}_{1-x}\text{As}$) or group V ($\text{GaAs}_{1-x}\text{P}_x$) sublattices [106]. Superlattice growth was also investigated for InGaAs/GaAs structures, in which signal oscillations with ML periodicity were used for real-time growth control. Fabry-Pérot interference effects were observed during the SL growths as an envelope to the RDS signals related to the growth of individual SL periods. A review article by Zorn *et al.* has also been published [107].

As discussed in Section 5.2, Arès *et al.* have also used RDS to study details of InAs SQW growth by ALE [90]. Extensions of this work have been carried out and will be described in Section 7.4. The next section will review published reports discussing PL characterization of InAs SQW structures.

5.4 Optical Properties of Ultrathin InAs Quantum Wells in GaAs

Apart from the interest in the InAs/GaAs system due to the fundamental materials properties and epitaxial growth challenges, there is considerable interest in the optical properties of these heterostructures. This is partly due to the fact that carriers bound to single and subML InAs depositions in GaAs represent an extreme example of quantum confinement. Additionally, such systems have exhibited sharp and intense

PL which is highly desirable for the production of laser devices. In this section a brief summary will be given in order to introduce several mechanisms which contribute to the PL observed in these systems. This will be followed by a short review of the rather rich literature dealing with this subject.

Optical characterization of epitaxial semiconductors is essential for identifying recombination mechanisms, studying band alignment or for simple evaluation of material quality. A PL measurement involves three principal processes: excitation, thermalization and recombination [108]. A laser light source with an energy greater than the bandgap energy, E_g , of the sample is used for excitation, in which electron-hole pairs are created in the material. These may then thermalize and relax towards quasi-thermal equilibrium distributions before recombining. Radiative recombinations produce the observed PL signal. A careful examination of the spectra may then be used to identify the responsible mechanisms based on emission energies and other properties of the spectra.

In pure materials at low temperature and low excitation levels electron-hole pairs are attracted to each other by Coulomb interactions to form excitons which can move throughout the material and transport energy [108]. The energy of a free exciton, E_{FE} , may be expressed as

$$E_{FE} = E_g - E_X + E_{KE} \quad , \quad (5.25)$$

where E_{KE} is the kinetic energy of the exciton. E_X represents the binding energy of the exciton, where

$$E_X = \frac{(13.6 \text{ eV})}{n^2} \frac{\mu}{m_0 \epsilon^2} \quad , \quad (5.26)$$

in terms of the dielectric constant of the material, ϵ , the electron mass, m_0 , and the principal quantum number, n . The Bohr energy is $m_0 e^4 / (4\pi \epsilon_0)^2 2\hbar^2 = 13.6 \text{ eV}$, where $\hbar$ is Planck's constant, ϵ_0 is the permittivity of free space and e is the electron charge. The reduced mass of the exciton is given by $\mu = m_e m_h / (m_e + m_h)$, where m_e and m_h are the electron and hole effective masses. For example, the $n = 1$ exciton binding energy in GaAs is approximately 5 meV, using the heavy-hole effective mass.

The binding energy of a free exciton can be increased by the presence of a point defect, like a neutral or ionized impurity in the material [108]. If the binding energy of

the exciton is increased near the impurity, then the exciton can minimize its energy by becoming bound to the defect. Bound excitons show sharp PL emission because the kinetic energy term in Equation 5.25 vanishes. In GaAs, PL lines are often observed arising from excitons bound to neutral acceptor and donor impurities. These are labelled ($A^0.X$) and ($D^0.X$) and at temperatures near the boiling point of liquid ^4He (4.2 K), these transitions have emission energies of 1.512 eV and 1.515 eV, respectively. The recombination energy for a bound exciton, E_{BE} , is given by the expression

$$E_{BE} = E_g - E_X - E_{Loc} \quad , \quad (5.27)$$

where E_{Loc} is the impurity-specific localization energy.

Figure 5.7: Illustration of radiative transitions involving electrons bound to neutral donors (D^0) and holes bound to neutral acceptors (A^0). CB and VB refer to the bottom and top of the conduction band and valence band, respectively.

Real materials contain both donor and acceptor impurities as illustrated in Figure 5.7. Under equilibrium conditions some electrons from the donors will be trapped by the acceptors. This produces ionized acceptors (A^-) and donors (D^+) in the material. Under optical excitation some of these ionized impurities may be neutralized

by the creation of additional electrons and holes. In returning to equilibrium some of the electrons bound to neutral donors will recombine with holes bound to neutral acceptors, resulting in the emission of so-called donor-acceptor-pair (DAP) luminescence ($D^0-A^0 \rightarrow D^+-A^-$). In MOVPE GaAs, in which carbon is a shallow acceptor (occupying As crystal sites), low-T PL spectra often exhibit DAP and free-bound ($e-C^0$) transitions at 1.490 and 1.493 eV, respectively.

InAs SQWs in GaAs are an example of isoelectronic δ -doping in semiconductors [109]. InAs and GaAs are both direct gap semiconductors with 4.2 K bandgaps of 0.418 eV and 1.519 eV, respectively [53]. Heterostructures of this type have a “straddling” band lineup (type I) in which the electron and hole are both quantized in the narrow-gap material. While this quantization occurs primarily in the InAs layer, the exciton dimensions are actually significantly larger than the InAs well-width, meaning that much of the exciton wavefunction extends into the GaAs barrier layers. The free exciton Bohr radius is given by $a_B^X = (\epsilon m_0/\mu)a_B^H$, where $a_B^H = 4\pi\epsilon_0\hbar^2/m_0e^2$ is the Bohr radius of the Hydrogen atom (0.529 Å). In GaAs the value is approximately $a_B^X = 111$ Å. In the case of an exciton confined to a quantum well the binding energy is increased, while the Bohr radius is reduced by the confinement. An interesting feature of excitons in quasi 2-dimensional systems is the splitting into light- and heavy-hole excitons resulting from the corresponding splitting of the valence-band states [109]. Under normal conditions the heavy- and light-holes are degenerate at the centre of the Brillouin zone. The lifting of this degeneracy is illustrated in the schematic of the InAs/GaAs band alignment given in Figure 5.8.

Many published reports have discussed PL emission from excitons bound to ML or subML InAs SQWs in GaAs. Experimental studies have involved samples grown using MBE [10, 11],[13]-[15],[110]-[123], MEE [12, 110], ALE [5, 124] and FME [79]. Very few articles have dealt with films grown by conventional MOVPE [7],[125]-[127]. To illustrate the differences in the results obtained by various researchers, Table 5.2 gives the PL emission energies and linewidths (where available) for InAs films with thicknesses near 1 ML. Thicker and thinner films have also been studied. Similar discrepancies (or similarities) have been observed and in general the emission energies of subML films are higher than those of 1 ML films, while the linewidths are generally

Figure 5.8: Illustration of band alignment in InAs/GaAs SQW structures (from Brandt [10]). The figure shows both the k -space band structure and the real-space line-up. The unstrained band structures for InAs and GaAs are given in the left and right parts. The dashed lines illustrate the shift of the InAs band edges due to the compressive strain, leading to the situation shown in the middle. The inset shows a magnification of the heavy-hole (hh) and light-hole (lh) states and the optical transitions, indicated by arrows.

narrower. For thicker films the converse is generally true.

SubMLs of InAs in GaAs were studied by numerous authors [5],[13]-[15], [116, 117, 119, 121, 123]. These studies demonstrated the sharp and intense luminescence which can be obtained by burying very small amounts of InAs within a GaAs matrix. However, no consensus has been reached on either the structural properties of the films or the nature of the optical emission. It was believed that the InAs forms island arrays which are oriented along the $[01\bar{1}]$ -direction [15]. This islanding postulate was based on the absence of excitonic resonances in samples in which the growth was interrupted after the InAs layer deposition, which was thought to promote a uniform subML coverage. The orientation of the islands was postulated due to the anisotropy of the luminescence with polarized excitation illumination. Islanding of the InAs was believed to be a suitable mechanism for producing 0-dimensional quantum confinement [14], although more recent work has found that the PL results may be adequately explained by 2-dimensional well-models, since InAs islands are much smaller than the exciton radius [5, 123]. In this case the subML film is treated as a conventional quantum well, with its interface roughness determined by the average InAs coverage. For subML depositions it was found that the PL emission energies increased with decreasing InAs coverage, while the linewidths generally decreased [5, 123]. Eventually the InAs-related luminescence merges with the GaAs bound excitonic features for very low coverages.

Light-emitting devices, e.g. laser structures, using InAs/GaAs active regions have been produced by several groups, using MBE [11, 128], ALMBE [12] and MOVPE [7, 126]. Of these, some devices contained InAs SQWs in GaAs [7, 11, 12], while others contained $(\text{InAs})_n/(\text{GaAs})_m$ short-period superlattices (SPSLs) with $(n, m) = (1, 2)$ [126] and $(n, m) = (1, 4)$ [128]. It is likely that the SPSL structures actually consisted of InGaAs alloy films in the active regions due to segregation. The most recent laser results are particularly interesting due to the excitonic nature of the light emission and the high efficiency [7]. It is noteworthy that continuous wave (CW) operation of an injection-type laser employing an InAs single- or subML active region has not been demonstrated, to the best of our knowledge.

Recent theoretical developments have reemphasized the promise of ultrathin InAs

SQWs in GaAs for highly efficient luminescence [6, 129]. Empirical tight-binding (ETB) calculations were used, and were thought to be suitable for this type of system because (i) the only input parameters are the band-structure values of the substrate and substitution bulk materials (e.g. GaAs and InAs), and (ii) ETB is an atomistic model and makes no assumption on the shape of the wave function or the interface matching conditions [129]. In the most recent calculation, Iotti *et al.* used a Green's function tight-binding model, in which the exciton is Wannier-Mott like in its in-plane dynamics [6]. Along the growth direction the electron-hole dynamics were treated by tight-binding, thus taking the band-folding along the growth direction into account. The band-folding results in a larger effective mass for both types of carriers. Measuring energies from the top of the GaAs valence-band, this calculation predicted heavy-hole and CB levels bound at 23 and 1468 meV for 1 ML InAs insertions. The corresponding localization energy of the ML CB measured from the bottom of the GaAs CB was predicted to be 52 meV. The study also suggested that the exciton has a binding energy of 12.9 meV and so excitonic effects should be observable at room temperature. Additionally, the oscillator strength per unit area was predicted to be $12.9 \times 10^{12} \text{ cm}^{-2}$ which is between 3 and 5 times as large as the oscillator strength in an $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QW 80 Å wide [6]. These enhancements arise because of the increased wave-function localization, large in-plane masses and in-plane nonparabolicity, all of which tend to increase the binding energy and the oscillator strength.

In this chapter it has been shown that the InAs/GaAs system has been the subject of considerable research recently. Various issues have been discussed, including the structure and epitaxial growth of ultrathin films with thicknesses below the critical thickness, beyond which the growth becomes three-dimensional in nature. In fact, growth in the (3-D) Stranski-Krastanov regime and films produced by this mechanism are also the subject of extremely intense study at this time. In this chapter growth methods for avoiding In segregation have been discussed, and will allow an interpretation of the experimental data presented in Chapter 7. Similarly, optical characterization using *in-situ* RDS and *ex-situ* PL measurements have been discussed in order to create a context for the related work which has been performed in this thesis. Chapter 6 will now describe the experimental methods employed in this work.

Ref.	Description	t [ML]	T [K]	E_{PL} [eV]	Γ_{PL} [meV]
[5]	ALE SQWs, flashoff	1	1.8	1.460	7
[7]	MOVPE laser structure	1.5	2	1.12	10
[10]	MBE SQW, flashoff	1.2	4.2	1.417	22
[11]	MBE laser structure, $T_g = 550$ °C	1	77	1.477	-
[13]	MBE SQW, flashoff	1	8	1.441	8.0
[14]	MBE subMLs, flashoff	0.8	6	1.465	-
[15]	MBE SQWs, flashoff	1	5	1.463	-
[79]	FME SQW, $T_g = 500$ °C, AsH ₃	1	2	1.483	3.2
[84]	ALMBE SQW, $T_g = 360$ °C	1	10	1.454	-
[84]	ALMBE SQW, $T_g = 460$ °C	0.9	10	1.479	-
[84]	MBE SQW, $T_g = 420$ °C	1	10	1.444	-
[84]	MBE SQW, $T_g = 480$ °C	1	10	1.459	-
[110]	MEE SQW, $T_g = 350$ °C	0.9	10	1.48	6
[110]	MBE MQW, $T_g = 550$ °C	1.2	10	1.45	8
[111]	MBE MQW, flashoff	0.8	4.2	1.47	5
[112]	MBE MQW, flashoff	0.8	4.2	1.47	-
[113]	MBE SQWs, $T_g = 420$ °C	1	-	1.461	-
[114, 115]	MBE SQWs, $T_g = 380$ °C	0.92	6	1.442	7.5
[114]	MBE SQWs, $T_g = 430$ °C	0.92	6	1.452	5
[114]	MBE SQWs, $T_g = 480$ °C	0.92	6	1.47	2.5
[121]	MBE, $T_g = 400$ °C, cap at 580 °C	1	11	1.43	-
[122]	MBE SL, 10 periods, $T_g = 500$ °C	0.85	10	1.478	6
[123]	MBE SQWs, flashoff	1	10	1.4635	9.5
[125]	MOVPE SQWs, $T_g = 730$ °C, AsH ₃	1.03	4	1.491	5
[127]	MOVPE SQW	1	5	1.472	6

Table 5.2: Experimental PL energies, E_{PL} , and full-widths at half maxima, Γ_{PL} , reported for InAs/GaAs heterostructures, measured at temperature, T . The thicknesses of the InAs layers, t , are given in units of MLs, as quoted by the authors. The definition of the thickness of a strained InAs layer in GaAs(001) is not consistent among all authors.

Chapter 6

Experimental Details

In this chapter the details of the MOVPE technique will be presented. This will be followed by a discussion of the *in-situ* and *ex-situ* characterization which was carried out at SFU. Sections 6.6 and 6.7 will then describe the setups used at the various synchrotron beamlines used in these experiments.

6.1 The MOVPE System

The MOVPE system used in this research was manufactured by Thomas Swan and includes a commercial gas handling unit and computer-control software [16]. An illustration of the system appears in Figure 6.1. Ultrahigh purity (UHP) hydrogen is used as the carrier gas, while liquid nitrogen (LN_2) is evaporated to provide the vent-line gas supply. Reactor gases travel through high purity stainless steel tubing, making use of VCR^{TM} connectors to provide metal, as opposed to elastomer, seals.

As mentioned in Chapter 2, the stainless steel bubblers containing the metalorganic sources are maintained at constant temperature using ethylene glycol baths. The bubbler pressures are controlled electronically to provide stable, reproducible conditions. During a growth sequence H_2 gas is passed continuously through the relevant bubblers to achieve steady-state conditions. The run-to-vent switching system enables the saturated group III or group V vapours to be directed to carrier or vent lines as required by the growth recipe. Separate alkyl and hydride carrier lines are

Figure 6.1: A schematic of the vertical MOVPE reactor and associated gas flow lines. The figure includes the RDS system which allows *in-situ* characterization of the growing films.

used to prevent intermixing between the saturated vapours.

Several techniques are employed by the system to ensure steady, laminar reactor flows. The total gas flow passing through both carrier lines is kept constant by a computer-controlled makeup flow. During run-to-vent gas switching, the makeup line compensates for the reduced amount of gas to preserve the total flow of the line and hence to avoid turbulent flows. Additionally, the run and vent lines are kept at equal pressures using a differential pressure controller which makes small adjustments to the vent flow as required.

The vertical growth reactor employed in this work features stainless steel construction with continuous water cooling. The design is similar to that described by Brennan *et al.* with optical ports for normal incidence and Brewster angle measurements [104]. Carrier lines enter the top of the chamber while purge lines are used to maintain laminar flow in the reactor and to keep the optical windows clean. The carrier gases mix in the top of the reactor and travel downwards through a quartz nozzle which directs the saturated vapours in a laminar flow pattern towards the susceptor and aids in reducing the quantity of wasted material. The volume surrounding the cylindrical nozzle is purged with hydrogen gas to assist in maintaining laminar flow. A summary of the growth conditions appears in Table 6.1. The next section describes the RDS system shown in Figure 6.1.

Parameter	ALE	MOVPE
Reactor pressure	50 Torr	50 Torr
Alkyl total flow	500 sccm	250 sccm
Hydride total flow	500 sccm	250 sccm
Total gas flow	4.6 slm	2.3 slm
Window purge flow	20 sccm	20 sccm
Gas velocity	50 cm s^{-1}	25 cm s^{-1}

Table 6.1: Summary of ALE and MOVPE growth conditions.

6.2 RDS Measurements

The RDS apparatus is mounted on a vertical optical table above the reactor chamber to allow normal incidence measurements. An extensive discussion of the RDS technique has been given by Arès [16]. Light is produced by a Xe arc lamp and directed onto the sample's surface using front surface focusing optics. The path from the lamp to the sample contains a MgF_2 Rochon prism which polarizes the light. The linearly polarized light is then incident upon the sample at 45° to the principal crystal axes (the crystal directions (110) and $(\bar{1}10)$). The electric field components along these two directions are initially equal. The reflected light has different components along the two directions because of anisotropy on the sample surface.

Figure 6.1 shows the photoelastic modulator unit which is part of the system for analyzing the reflected light. The photoelastic modulator contains a quartz bar which becomes birefringent under stress induced by a piezoelectric cell. This stress is modulated at 50 kHz using an electronic controller to produce retardations between $-\lambda/2$ and $\lambda/2$. The main axis of the photoelastic modulator is positioned to coincide with the polarization direction of the light prior to reflection. The components of the polarization of the reflected light are analyzed using a quartz Rochon prism. Finally a 0.25 m grating spectrometer is used to monitor the signal with a photomultiplier tube having a wide spectral response multialkali photocathode.

The intensity of the light reaching the detector contains a bulk, isotropic signal and a small modulation due to the anisotropic surface. A lock-in amplifier is used to measure the amplitude of the modulated signal, which is about $10^{-4} - 10^{-5}$ times that of the DC component. An electronic control circuit is used to maintain a constant DC signal level by varying the gain (and hence the sensitivity) of the photomultiplier tube.

A full RDS spectrum (1.5 - 5 eV) cannot be taken sufficiently quickly to permit time-resolved measurements. During a standard growth sequence on GaAs, for example, it is often preferable to monitor the RDS signal at a fixed energy. As mentioned in Section 5.3, a suitable energy is 2.6 eV, which exhibits strong features related to transitions within As dimers along the surface [99]. RDS transient signals obtained in this way allow the observation of surface anisotropy developments with very high temporal resolution (8 Hz). This method is particularly useful for observing the crystal surface during ALE growth.

RDS spectra contain contributions not only from the surface, but from artifacts related to stress in the optical window, etc. It is possible to correct for these effects by recording a spectrum in which the sample is rotated 90° from its original orientation. This can be done at the beginning of a growth experiment and then used to correct the spectra obtained during the experiment. This is possible because

$$\left(\frac{\Delta r}{r}\right)_{opt} = \left(\frac{\frac{\Delta r}{r}(0^\circ) + \frac{\Delta r}{r}(90^\circ)}{2}\right) = \left(\frac{\frac{\Delta r}{r}_{sam} + \frac{\Delta r}{r}_{opt} - \frac{\Delta r}{r}_{sam} + \frac{\Delta r}{r}_{opt}}{2}\right) \quad (6.1)$$

where $(\Delta r/r)_{sam}$ and $(\Delta r/r)_{opt}$ are the contributions to the real part of the RDS

Figure 6.2: RDS data obtained in two orientations, ϕ , used for determining the background signal. The background may be removed from the data to obtain correct relative levels.

signal due to the sample and the optics, respectively. An example of this process is shown in Figure 6.2.

In order to evaluate the development of surface anisotropy during the MOVPE growth of InAs QWs in GaAs, the real-time spectroscopic method of Aspnes was employed [101]. As described in Section 5.3, this exploits the reproducibility of a given growth sequence to obtain time-resolved data throughout the spectral range of interest. A single transient signal at fixed energy was recorded for each cycle of a GaAs/InAs SL growth on GaAs(001). The data were then reorganized to provide details of the surface anisotropy throughout a single growth cycle. The results will be presented in Section 7.6.1. The next section describes the atomic force microscopy measurements which form an important part of the *ex-situ* sample characterization performed at SFU.

6.3 Atomic Force Microscopy

After preparing an epitaxial sample it is useful to study the physical morphology of the sample surface. This can be done on different length scales using the naked eye, optical, atomic force or scanning tunnelling microscopes. This section will describe the AFM technique which is suitable for studying areas on the sample surface from $100 \times 100 \mu\text{m}^2$ to $1 \times 1 \mu\text{m}^2$ with relative ease. Higher-resolution scans, even at the atomic scale, are also possible but are more difficult.

Figure 6.3: A schematic of the atomic force microscope. 'A' and 'B' refer to the two PSPD elements. The inset shows the interaction between the AFM tip and the sample surface. The contact mode was used to obtain the images presented in this thesis.

AFM uses a cantilever upon which is mounted a sharp tip which is placed near the sample surface (Figure 6.3). Interactions between the tip and the surface produce

measurable changes which are used to study the surface. These interactions are illustrated in Figure 6.3. In this work, measurements were made in the “contact” mode. Here the tip comes in intimate contact with the sample surface (a few angstroms) and experiences a repulsive force. A visible laser beam deflects off the cantilever towards a position-sensitive photodetector (PSPD). Using a piezoelectric stage, the sample is rastered beneath the tip while the deflections are measured using the PSPD and an electronic feedback mechanism. In the measurements described here, the system was operated so that a constant force was applied to the tip. Changes in the surface topography produce changes in the PSPD signal which result in the adjustment of the height of the piezoelectric stage. The size of the necessary adjustment provides information on the height of features in the surface. Atomic scale imaging requires the constant height mode, where the spatial variation of the cantilever deflection is used directly to generate the topographic image.

6.4 PL Spectroscopy

The PL measurements included in this thesis were performed by Dale Harrison, working in Dr. Michael Thewalt’s laboratory. A more detailed discussion of the technique may be found in Dr. Harrison’s Ph.D. thesis [108].

Briefly, a PL system consists of four main components: a light source, a cryogenic dewar, a spectrometer and a detector. In this work the samples were mounted on a holder which was then immersed in the “tail” of a Janis immersion cryostat. The dewar system was precooled using LN_2 approximately 24 hours before the measurements were taken. Liquid helium (L^4He) was later introduced into the chamber to allow low temperature measurements (4.2 K). Measurements of the vapour pressure were obtained using a calibrated pressure gauge which allowed a determination of the L^4He bath temperature.

The tail of the dewar contains four quartz windows for sample excitation and signal acquisition, as illustrated in Figure 6.4. In this work the samples were illuminated by an Ar^+ -ion laser in CW operation. PL signals were measured using a Bomem DA8 Fourier transform spectrometer. This is essentially a Michelson interferometer.

Figure 6.4: a) Liquid He cryostat used in PL measurements. b) The geometry for sample illumination and signal acquisition. From Reference [108].

Interferograms were obtained as a function of path difference between the two branches of the interferometer. The data were then converted to intensity versus energy spectra using the Fast-Fourier Transform (FFT) algorithm. In the data presented in this thesis the intensity of the PL signals were recorded using a Si avalanche photodetector [108].

In the following sections the X-Ray techniques used in this work will be discussed. The first section will describe the method used in XRD measurements using a Cu anode source at SFU. This will be followed by details of the synchrotron measurements performed elsewhere.

6.5 High-Resolution XRD

In the SFU laboratory XRD measurements are routinely used to determine growth rates, sample composition and layer quality. A BEDE D³ (direct-drive diffractometer) system is used for the measurements in conjunction with a Philips generator and BEDE software for computer control. Cu-K X-Rays (the Cu K _{α_1} wavelength is 1.54056 Å (8047.78 eV)) are produced by a Philips long-fine-focus vacuum tube (usually operated at 40 kV and 30 mA) and are detected using a BEDE enhanced dynamic range (EDR) detector after diffraction. A schematic of the system is shown in Figure 6.5.

The BEDE system allows the incident X-Rays to be collimated in two modes, allowing high intensity, low-resolution or lower intensity, high-resolution measurements. This is accomplished using a pair of channel-cut crystals, each of which contains two separate channels for asymmetric or symmetric reflections. These crystals also act as a monochromator (MC), choosing Cu-K _{α_1} radiation. In the high intensity mode, two asymmetrically cut Si (220) crystals are used with a total of four reflections (angular divergence ~ 12 arcsec). The high-resolution mode uses eight reflections from two symmetric Si(220) crystals (angular divergence ~ 5 arcsec). After Bragg collimation the X-Ray beam is shaped by a fixed entrance slit which defines the beam in the x and y directions.

In the alignment of rocking curve measurements, the coarse motions of the sample and detector are adjusted by θ and 2θ stages, which control movements of the order of degrees. Fine adjustments and the actual measurements are performed using precision motors for movements of the order of arcseconds. These are sometimes referred to as ω and 2ω motions. To align the sample for the measurement of what are typically very narrow rocking curves, it is necessary to adjust the sample position by rotating about an axis parallel to the sample diffracting planes and the (horizontal) plane of incidence. The alignment is achieved through an iterative optimization process employing movements about this axis and ω -motions. Meanwhile, the rocking curve width and intensity are monitored by the detector. For GaAs crystals the symmetric (004)-reflection is typically observed to have a full-width at half maximum (FWHM)

Figure 6.5: The BEDE D³ system. The inset shows the high-intensity configuration in which the beam is collimated by two asymmetric Si(220) reflections in each channel-cut crystal.

of 8 arcsec and 16 arcsec for the high and low-resolution modes, respectively.

Rocking curves obtained in this way are compared with dynamical diffraction simulations using the BEDE RADS software. The software is quite versatile and is suitable for use with group IV and III-V zincblende semiconductors, including ternary and quaternary compounds. Simulations are prepared by defining the composition and thickness of the epitaxial layers beginning with the substrate and working upwards. The substrate thickness is assumed infinite as discussed in Section 3.3. RADS can be used with arbitrary reflections and with either σ or π polarizations or a combination of the two, which is most appropriate with a Cu-anode. To include the effects of the channel-cut crystals it is possible to include a correlation function. The rocking curve for the sample is initially calculated over a range double that specified by the user. This prevents convolution artifacts at the edges of the desired range. The rocking

curve correlation function due to the channel-cut crystals is then calculated and convoluted with the sample curve to produce a realistic profile for the true arrangement over the specified range. It is important to note that the simulations are usually performed using a logarithmic scale for the reflectivity. Many of the interesting features in the diffraction patterns are only apparent when the data are presented in this manner.

In the following section the XSW measurement technique is described. While the same physics is responsible for the dynamical diffraction occurring in the case of X-Rays from a Cu-anode or from a synchrotron source, there are many features unique to the latter. This is particularly true in the case of the back-reflection Bragg geometry employed here.

6.6 X-Ray Standing Wave Measurements

XSW measurements were performed at NIST beamline X24A at the NSLS. This section provides a description of the apparatus and the techniques used in these measurements.

Synchrotron radiation results from the bending of electron (or positron) trajectories as the relativistic particles travel in closed circular orbits [130]. In practice a “bunch” of electrons is inserted into a UHV storage ring where they are accelerated to velocities approaching the speed of light. Around the ring, magnets are used to bend the electron paths, resulting in the emission of electromagnetic radiation. During the course of these experiments the NSLS storage ring was operating at 2.6 GeV. Shortly after the injection of electron bunches into the ring, the electron current was typically about 300 mA. During the twelve hours before the next injection, this current decayed slowly to approximately 150 mA. The decay rate was sufficiently slow to be negligible during the course of a single spectrum acquisition (~ 15 minutes). The photons are actually emitted in pulses of nanosecond duration, but for the purposes of most experiments the radiation is essentially continuous.

The radiation produced at a synchrotron source encompasses a broad spectral range, from microwaves to hard X-Rays and γ -Rays. The natural collimation of the

emitted radiation has the advantageous property that it is confined to a narrow range of vertical angles, centred at the plane of the reference electron orbit. In the plane of the orbit the radiation is linearly polarized, while it is elliptically polarized elsewhere. One of the most attractive features is the high photon flux, which is essential for measurements of extremely dilute samples, such as the In MLs and subMLs considered here.

In beamline X24A, "white" light from the ring enters the beamline and travels downstream towards the experiment with no vacuum interruptions. For the energies employed in this study (~ 4386 eV), the typical beryllium windows were not suitable and were not present anywhere in the beampath. At these energies the attenuation due to the windows would be excessive, thus the entire beamline operates under high vacuum of approximately $10^{-8} - 10^{-9}$ Torr.

The white X-rays were collimated by a Ni-coated spherical Al mirror located 6.8 m from the source, and then incident on the monochromator, 0.9 m further downstream. These experiments used a pair of Si(220) MC crystals as shown in Figure 6.6. With this configuration the energy resolution was approximately $\Delta E/E = 5 \times 10^{-5}$ at ~ 4386 eV. The motion of the crystals was controlled by stepper motors interfaced to a Digital Equipment Corporation PDP11/73 microcomputer.

Approximately 4 m upstream from the experiment the monochromatic X-rays were collimated in the x and y directions by a pair of adjustable slits. Finally a fixed entrance slit ~ 1 m upstream from the experimental chamber cut the beam down to approximately 1.5 mm (vertical) $\times$ 10 mm (horizontal).

The semiconductor samples were mounted within a stainless steel vacuum chamber as shown in Figure 6.7. The chamber was evacuated by a combination of rotary, turbomolecular and ion pumps (not depicted in the figure), with the pressure monitored by an ion gauge and a quadropole mass spectrometer. The vacuum components were interlocked so that a local vacuum failure would not vent the entire storage ring to atmosphere.

Sample alignment was accomplished using a manipulator mounted on a linear bellows and attached to the aluminum base upon which the samples were mounted. The manipulator rod was constructed from Macor to allow the aluminum base to be

Figure 6.6: A schematic of the experimental back-reflection XSW arrangement at beamline X24A at the NSLS (not to scale).

electrically isolated from the chamber. No azimuthal adjustments were possible with this apparatus.

As shown in Figures 6.6 and 6.7, the relative incident and reflected beam intensities were measured by monitoring the current, I_0 , through a fine Ni mesh between the entrance slit and the sample. The current signal was passed by coaxial cable to a preamplifier placed very close to the mesh, and then to a voltage/frequency converter.

The true sample configuration differed slightly from the ideal back-reflection geometry. The entrance/exit slit depicted in Figure 6.7 was coated in phosphor to permit visual observation of the incident and reflected beams; the phosphor glowed bright green under X-ray illumination. At the GaAs(004) back-reflection, the incident beam was observed to pass through the entrance slit, while the back-reflected beam passed

Figure 6.7: A schematic of the experimental chamber used in XSW measurements at the NSLS.

through a second slit 5 mm above. With a slit-sample distance of approximately 1 m, this corresponds to a (negligible) deviation from the ideal geometry of about 0.3° .

As illustrated in Figure 6.7, the XSW signal from the substrate was monitored through measurements of the total electron yield (TEY). A wire connected to the aluminum sample mount was passed to a nearby preamplifier, with the resulting current signal carried to a voltage/frequency converter.

The fluorescence detector employed in these measurements was a CANBERRA Model GUL0110P Ultra Low Energy Germanium PIN diode with an active area of 100 mm^2 . As shown in Figure 6.7, the detector was introduced into the experimental chamber using a linear translation stage with bellows. Detector cooling was achieved with a LN_2 cryostat/cold finger assembly to reduce thermal noise.

A schematic of the detector and associated electronics is shown in Figure 6.8. Under reverse bias, the $\text{P}^+(\text{B})\text{-I-N}^+(\text{Li})$ Ge homojunction is sensitive to ionizing radiation incident in the intrinsic region. The atomic symbols in parentheses denote the dopant in each Ge layer. The energy of each deposited photon results in the production of a proportional number of charge carriers, which are swept by the bias voltage into the P and N electrodes. This signal is then converted to a voltage pulse by the integral charge-sensitive preamplifier.

Element	$L_{\alpha 1}$ [eV]	$L_{\alpha 2}$ [eV]	$L_{\beta 1}$ [eV]
Ga	1097.92	1097.92	1124.8
As	1282.0	1282.0	1317.0
In	3286.94	3279.29	3487.21

Table 6.2: X-Ray emission energies (from Bearden [131]).

Figure 6.8 shows the Be and the polymer/Aluminum windows mounted to the detector. The former was mounted specifically for these experiments to reduce the fluorescence signal due to Ga and As in the samples. Fluorescence energies for the elements of interest and within our detection range are given in Table 6.2. The attenuation of X-rays in matter can be expressed as

$$I_t = I_0 e^{-\mu t} , \quad (6.2)$$

Figure 6.8: The Ge fluorescence detector and NIM electronics used in X-ray standing wave measurements.

where I_0 and I_t are the incident X-Ray intensity and the intensity at a depth, t , in the material. Here μ is the linear absorption coefficient. From Figure 6.9 it is apparent that a window of thickness $50.8\text{ }\mu\text{m}$ (2 mil) causes significant attenuation of the Ga and As fluorescence, with minimal attenuation of the In fluorescence. The polymer window supplied by the manufacturer is used to improve the detector efficiency in the range 2-30 keV, and results in a nearly “flat” response in this region. Silicon ribs (0.3 mm thick, $100\text{ }\mu\text{m}$ apart, $20\text{--}25\text{ }\mu\text{m}$ wide) are used to support the polymer under vacuum and provide tight collimation of the photons incident on the Ge element.

Figure 6.9: The transmission of X-Rays through a Be window of thickness $50.8\text{ }\mu\text{m}$.

The detector signal from the preamplifier was passed through a cable transformer which reduces high frequency interference and into the amplifier in the nuclear instruments module (NIM) bin. This amplified analog signal was passed simultaneously to the analog-to-digital converter (ADC) and to a group of four single-channel analyzers (SCAs) in parallel (Figure 6.8). The ADC output was monitored by a multichannel analyzer (MCA).

The energy range monitored by the detector is determined by the applied bias

voltage and gain set at the high-voltage power supply (HVPS). For these experiments the range extended from 0 to approximately 6000 eV. The ADC output to the MCA allowed the observation of the measured detector counts in real time. More importantly, the MCA was used to set the energy windows for the four SCAs as follows. Consider a typical MCA spectrum as illustrated in Figure 6.8. Four peaks were observed and associated with the following emission lines: Ga, As $L_{\alpha,\beta}$; In $L_{\alpha,\beta}$; and X-ray elastic scattering. This identification was based on a detector calibration obtained using an indium ingot mounted in the sample position. The fourth peak is related to the pulser reference signal and will be discussed presently.

By gating each SCA with the ADC signal individually, and in the coincidence counting mode, it was possible to isolate the energy window associated with the SCA for observation on the MCA. The energy level and the window width were then adjusted to the desired bandwidth. Thus the four SCAs were set to measure the In fluorescence; the total detector fluorescence; the Ga and As fluorescence; and the pulser signal.

The pulser reference signal to the detector “test” input was used to monitor the dead time of the detector. By supplying a regular signal with well-defined frequency and amplitude, it was possible to ensure that the detector did not become saturated at the GaAs(004) Bragg condition, when the number of fluorescence counts became quite large. Indeed, the pulser signal measured by the detector was observed to remain quite flat throughout the energy range of the experiments.

Each sample was aligned in the sample chamber by optimizing the sample position to find the back-reflection Bragg peak in the reflectivity and the XSW pattern in the TEY. For each sample approximately twenty scans were recorded, over a range of 4381 to 4391 eV in steps of approximately 0.064 eV and with a count time on the order of 5 seconds per step. The data were then summed together to obtain good statistics as described in Section 7.1. In the next section the XAFS measurements at SSRL will be described. By combining the XSW and XRD measurements with XAFS, which studies the local environment of an absorbing atom, it is possible to develop a more complete structural understanding of the InAs SQWs.

6.7 Grazing Incidence XAFS

This section describes the equipment and the methods which were employed in the XAFS measurements performed at SSRL. Following a description of the SSRL-designed grazing incidence X-Ray absorption spectroscopy (GIXAS) apparatus [132], the method of alignment and data acquisition will be outlined. This includes both reflectivity and XAFS measurements, which were performed in the polarization-dependent near-total reflection mode at the In K-edge (27940 eV).

XAFS measurements were made at SSRL beamline 4-2 with the storage ring operating at an electron energy of 3 GeV and a stored current in the range of 100-65 mA. Data were collected with a Si(220) double-crystal MC, with an entrance slit width of 1 mm and no beam focusing. Under these conditions no detuning was used. All XAFS measurements described in this thesis were performed at room temperature.

A schematic of the GIXAS stage is given in Figure 6.10. The apparatus uses 18 motors interfaced to the beamline VAX system. Three motors on the rail, along with the hutch vertical table motion, were used for two-point alignment of the beam. Each Huber slit set consists of a pair of blades in both the vertical and horizontal directions. S1 and S2 were used for defining the incident beam, while S3 was used for alignment and during reflectivity scans. The sample position was controlled by three motors defining the grazing angle, θ ; the azimuthal angle, ϕ ; and the vertical position, z .

The X-ray intensity before and after the sample was measured using the ionization chambers, I_0 and I_1 , respectively. These were filled with argon gas at a pressure slightly greater than 1 atm. The currents were measured using picoammeters with a gain of 10^{10} amps/Volt.

Element	$K_{\alpha 1}$ [eV]	$K_{\alpha 2}$ [eV]	$K_{\beta 1}$ [eV]
Ga	9251.74	9224.82	10264.2
As	10543.72	10507.99	11726.2
In	24209.7	24002.0	27275.9

Table 6.3: X-Ray emission energies (from Bearden [131]).

Figure 6.10: The SSRL GIXAS stage. The whole apparatus is rotated 90° about an axis parallel to the beam path for measurements in the perpendicular polarization.

In K_α -fluorescence excitation from the samples was measured using a 13 element Ge solid state detector, similar to the one used for XSW measurements but with a much larger active surface area. The electronics instrumentation for each detector element was equivalent to that used for the single element detector described in Section 6.6. To reduce the total incoming count rate signal from the Ga and As fluorescence, two Al filters of thickness 0.75 mm were placed in front of the detector. The energy dependence of the transmission is shown in Figure 6.11. From the figure it is apparent that the Ga and As fluorescence is strongly reduced by the filters. A guideline for the setup was to keep the total incoming count rate in each detector channel

below about 3×10^4 counts/s. Beyond this level saturation of the detector becomes a concern. The energies of the K-fluorescence lines for the elements of interest are given in Table 6.3.

Figure 6.11: The transmission of X-rays through a 1.5 mm Al filter.

Alignment of the GIXAS stage with the beam was accomplished in a straightforward way using the upstream (US) and downstream (DS) rail motions. For the reflectivity and XAFS measurements the following procedure was used. The Huber slits were set to the desired aperture, which differed between the $E_{\parallel}$ and $E_{\perp}$ configurations, due to the asymmetry of the beam footprint. The “vertical” beam height was limited by the sample size and geometry as will be discussed. The sample height, z , was increased until the I_1 beam intensity was equal to half of the full-beam value, indicating that the sample was eclipsing the beam. The glancing angle, θ , was then optimized to its centre position. The sample height and angle were then optimized iteratively with respect to one another [132].

Figure 6.12 depicts the X-Ray beam illuminating a sample in the GIXAS geometry. The samples measured in this thesis consisted of 1/4 sections of a 2” diameter round

Figure 6.12: The experimental GIXAS geometry.

wafer, and so had a maximum length of approximately $L = 25.4$ mm. From the geometry it is clear that a beam height of $h = L \sin \theta$ would be just sufficient to illuminate the whole sample surface. At 200 eV above the In-K edge the critical angle is $\theta_C = 90$ mdeg, for which the appropriate beam height is $40 \mu\text{m}$. To study In layers buried beneath ~ 100 Å of GaAs it was necessary to make XAFS measurements at $\theta = 220$ mdeg which required a correspondingly larger beam height. In most of the measurements we used $h = 300 \mu\text{m}$.

For the reflectivity geometry, the top vertical blade of S3 was raised to admit the reflected beam. With the sample lowered out of the beam path, the lower S3 blade was then raised to occlude the straight-through beam and the sample was returned to its optimum position. Reflectivity measurements were performed by scanning the glancing angle, while measuring the incident and reflected beam intensities and In K-fluorescence.

XAFS spectra were obtained by fixing the glancing angle and scanning in energy throughout a range which includes the In-K edge. The measurement ranges are shown in Table 6.4. For each sample approximately 15 “sweeps” of this type were used, each of which contains fluorescence data measured by the 13 element detector, normalized

Energy range [eV]	Stepsize [eV]	Count time [sec]
27740-27920	10	1
27920-27970	1.06	3
27970-28686.86 (2.81 Å ⁻¹ -14 Å ⁻¹)	1.08→5.33 (0.05 Å ⁻¹)	3

Table 6.4: The XAFS spectra were divided into three ranges. Coarse steps were used below the absorption edge. In the XANES region a finer mesh was used. In the EXAFS region the steps were defined in k -space, rather than in energy.

by the incident intensities. A technical nuisance which occurs in this type of measurement is the appearance of Bragg peaks in the XAFS spectra. By carefully observing the position of Bragg peaks in the XAFS spectra for each channel and rotating the ϕ stage of the sample, it was possible to move these peaks to the extremes of the spectra and sometimes to remove them altogether. Still, analysis of the XAFS data involves a lengthy process of “degitching” the spectra measured by each of the detector elements, for all sweeps recorded for each sample. The sweeps are then summed together to provide good statistics.

In the next chapter the experimental data will be presented. The chapter will describe the growth sequences employed in the MOVPE sample preparation and the characterization of the samples in the SFU laboratory and at the other facilities described in the preceding sections. Considerable attention will be given to the methods of data analysis and interpretation.

Chapter 7

Experimental Results

In the previous chapter the experimental systems were described. This chapter will give the details of the sample preparation for the MOVPE and ALE layers grown at SFU and also for an XSW study of MBE samples. Several groups of samples were prepared at SFU and characterized, both *in-situ* using RDS and *ex-situ* using HRXRD, PL, AFM, XSW and XAFS. These studies will be described separately and the main results will be presented. The chapter will begin by outlining the details of the XSW data analysis.

7.1 Analysis of Experimental XSW Data

7.1.1 Preliminaries

Before beginning the description of the XSW data analysis in InAs/GaAs samples, it is useful to consider results obtained using a GaAs(001) reference wafer. As described in Section 6.6, an XSW measurement for a single sample is obtained by taking multiple measurements and then summing the data to enhance the signal:noise and improve the experimental precision. A suite of C++ programs designed for the XSW analysis handle the preliminary processing of the raw data and ultimately use nonlinear least-squares fitting to determine the XSW coherent position, P^H , and coherent fraction, F^H , for the sample. Characteristic data after processing are shown in Figure 7.1.

Figure 7.1: Photon energy dependence of the reflectivity (bottom curve) for a reference epi-ready GaAs crystal near the GaAs(004) Bragg backreflection condition. The XSW patterns obtained by measuring the total electron yield and the Ga and As-L fluorescence yields are shown in ascending order, with fit parameters as indicated. The solid lines are the best fits to the data points and the curves were offset for clarity.

The figure shows the sum of a series of reflectivity scans for a bulk GaAs reference crystal near the (004) back-reflection condition. The semi-insulating (SI) substrate crystal was manufactured by American XTAL Technology (AXT) using the vertical gradient freeze (VGF) method. It is important to note that this epi-ready crystal was measured with no cleaning or processing. The XSW patterns were obtained using the total electron yield (TEY), and the Ga and As L-fluorescence yields (FLY). At the low energy side of the Bragg reflection the nodes of the XSW lie on the substrate planes. As the phase shifts throughout the Bragg peak the wavefield moves continuously until the antinodes lie on the substrate planes at the high energy side. The TEY and FLY spectra in Figure 7.1 are proportional to the absorption of the atoms in the field of the XSW and are used to deduce the spatial distribution of a given type of atom.

Raw datasets cannot be summed directly because the MC tends to exhibit a slight energy offset between consecutive scans. These offsets were accounted for using the following method. Each XSW dataset contains columns corresponding to the substrate reflectivity; the Ga and As FLY; the TEY; the In L-fluorescence (for samples containing In); the total FLY; and the pulser reference signal. For each scan the reflectivity, R , as a function of photon energy, E , was calculated using the DTXRD as discussed in Chapter 3. In this calculation the structure factors F_H and $F_{\bar{H}}$ were computed for the (004) and (000) GaAs substrate reflections using the method of Appendix A. Recall that for the symmetric Bragg case used in these measurements the polarization appearing in Equation 3.30 has the value $P = 1$, while the asymmetry factor, $b = -1$. For the backreflection geometry (Equation 3.47)

$$\eta = \frac{(-2\Delta E/E + \Gamma F_0)}{\Gamma[F_H F_{\bar{H}}]^{1/2}} \quad , \quad (7.1)$$

where $\Delta E = (E - \delta E) - E_B$, in terms of the MC energy offset, δE , and the Bragg energy, E_B . The reflectivity predicted by the DTXRD is then given by (Equation 3.33)

$$R = \left| \frac{F_H}{F_{\bar{H}}} \right| |b| |\eta \pm (\eta^2 - 1)^{1/2}|^2 \quad . \quad (7.2)$$

The experimental data cannot be fitted to this simple expression because of the spectral broadening of the beamline apparatus. The Si(220) MC crystals each have

a characteristic, finite, rocking curve which contributes to the energy spectrum of the “monochromatic” beam. To account for this divergence, the reflectivity given by Equation 7.2 is convoluted with a Gaussian which simulates the lineshape of the MC signal. (For a complete discussion of multiple crystal arrangements, see Reference [133].) The Gaussian has the form

$$G(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E - E_i)^2}{2\sigma^2}\right] . \quad (7.3)$$

Here σ is the standard deviation of the MC lineshape, while E_i is the nominal energy in MC steps, and E is the energy of a given point on the curve centred at E_i . The convolution is carried out by numerically integrating the convolution function $R'(E) = \int G(E')R(E + E')dE'$ over a range of E' equivalent to about 16σ . In the fitting program σ is a fitting parameter and the MC lineshape has a width $\text{FWHM} = 2.354\sigma$. Experimental values of σ near 0.09 eV were found, corresponding to $\text{FWHM} = 0.21$ eV.

The experimental reflectivity is then least-squares-fitted using the Marquardt algorithm [134] to the convoluted rocking curve, multiplied by a linear function of the form $(A + B(E - E_1))$ to account for the variation in the beam flux with energy. E_1 is the energy of the first point in the scan. Thus, each reflectivity dataset is fitted with the variable parameters: δE , σ , A , B and C to the expression

$$R_{fit}(E) = (A + B(E - E_1))(1 + CR'(E)) . \quad (7.4)$$

The signal measured by the Ni mesh is actually proportional to $(1 + CR'(E))$ because the incident and reflected beams pass through the mesh simultaneously. The final fit parameter, C , accounts for the intensity loss of the reflected beam in travelling from the crystal to the mesh.

Each single-scan reflectivity curve was fitted in this way and corrected to remove the energy offset. A 4th order polynomial interpolation [134] was then used to put the data back on their original “grid” in energy space. The other data (TEY, etc.) obtained in each scan were corrected using the same δE . Repeating this process for all scan datasets allowed the datasets to be added properly, without introducing significant systematic errors. To eliminate artifacts from the interpolation the energy range of the data was reduced by 1 eV at each extreme.

Figure 7.1 shows the reflectivity, the TEY and the FLY data for the reference GaAs crystal after following this procedure to remove the offsets and to sum the scans. A few points are noteworthy at this stage. The reflectivity curve does not exhibit the asymmetric Darwin-Prins shape (Figure 3.3) because of the convolution with the MC resolution function. The convolution of two or more crystal rocking curves generally produces this shape [133]. Secondly, the TEY and FLY curves are very well-defined. The random scatter associated with a measurement of N counts produces a statistical uncertainty, $\sqrt{N}$, in the measured values, about the mean value. From the figure the uncertainty may be roughly estimated by the scatter in the points, suggesting that the FLY spectrum has a quite low uncertainty ($\sqrt{N}/N \sim 1.3\%$ at E_1). The Ga and As FLY signals have poorer statistics than the In FLY signals used to measure the SQW samples because of lower counting times, and because of attenuation of the lower-energy signals by the Be filter (Section 6.6). The TEY signal exhibits no such scatter whatsoever, and has very good statistics ($\sqrt{N}/N \sim 0.4\%$ at E_1). In general, data were collected for sufficient times to allow a maximum statistical uncertainty in the In FLY of approximately 1%.

7.1.2 Standing Wave Analysis

After offset correction and the summation of a series of datasets the experimental data may be fitted to an expression describing the XSW. The reflectivity sum is first fitted using the same method as in the preceeding section to determine the level of any remaining offset, δE and the energy resolution parameter, σ . The fit parameters A , B and C are useful for linear background removal and normalization (this has been done for all of the data presented here). The offset and resolution are more important because they affect not only the reflectivity, but the other measured data as well.

The TEY or FLY XSW curves are fitted in the following way. The offset in the XSW data is corrected using the energy offset determined by the reflectivity fitting. The Gaussian broadening function is similarly calculated using the appropriate value of σ . Using Equation 3.53 the XSW yield is given by

$$Y^H(E) = 1 + R(E) + 2\sqrt{R(E)F^H} \cos(\alpha(E) - 2\pi P^H) , \quad (7.5)$$

with the fit parameters: P^H , which measures the coherent position of a particular type of atom relative to the substrate planes, normalized by the diffraction plane spacing, d_s , and the coherent fraction, F^H , which measures the δ -like nature of the atomic distribution perpendicular to the diffracting planes. The reflectivity, $R(E)$ and phase, $\alpha(E)$ of the substrate reflection are determined in the usual way. This expression is convoluted with the Gaussian function as before, i.e. $Y'^H(E) = \int G(E')Y^H(E + E')dE'$. Finally, the experimental data are least-squares-fitted to the convoluted XSW, multiplied by a linear function of the form $(A + B(E - E_1))$ to account for the variation in the beam flux with energy. Again E_1 is the energy of the first point in the scan. Thus, each XSW dataset is fitted with the variable parameters: A , B , P^H and F^H to the expression

$$Y_{fit}^H(E) = (A + B(E - E_1))Y'^H(E) \quad . \quad (7.6)$$

The error bars in the fit parameters P^H and F^H were determined using the residual sum of squares, defined as

$$\sum(sq) = \sum_{i=1}^N (y_i^{fit} - y_i)^2 \quad . \quad (7.7)$$

where y_i is the measured value of the i th data point and y_i^{fit} is the corresponding best-fit value. N is the number of data points. The quoted uncertainties indicate the values which double the squared residuals in each parameter while all other values were allowed to float.

Figure 7.1 shows the fitting results for both the TEY and FLY signals measured for the reference crystal. For this sample the expected values are $P^H = 1.0$ (corresponding to atoms situated on the (004)-planes), and $F^H = e^{-M}$, which is the Debye-Waller factor (~ 0.9) in GaAs [34]. The measured values (Figure 7.1) obtained using both types of emission (TEY, FLY) agree with one another and are close to the expected values. Lee *et al.* used the evanescent wave effect to measure a GaAs buffer layer underneath a single buried InAs layer in GaAs [4]. Their measured values of $P^H = 1.00 \pm 0.01$ and $F^H = 0.81 \pm 0.01$ are in good agreement with the present results. The depth sensitivity of the fluorescent photons is discussed in Reference [4]. In the

experiments described in this thesis, the average takeoff angle viewed by the detector aperture was greater than the critical angle for fluorescent X-Rays leaving the crystal (1.5° at the As- L_{α_1} energy, 1282 eV), with relatively little extinction, and so the FLY includes contributions from atoms at depths of hundreds of angstroms below the surface. Also, for the relatively low photon energies employed in this work the TEY signal should approximate a bulk site close to the crystal surface [135], and so the measured values are due to atoms on bulk sites within the crystal. This suggests that the Debye-Waller factor may be slightly smaller than 0.9 in these samples.

With this background in XSW analysis we now consider the XSW measurements of InAs SQW samples.

7.2 XSW Study of MBE-Grown Films

The first series of samples measured using XSW as part of this thesis work were studied in collaboration with NIST and Brooklyn College, NY in order to extend the structural understanding of InAs SQWs which had begun to form through earlier measurements [2, 3, 4]. These MBE films were prepared by Dr. Joseph Pellegrino and Dr. Joseph Woicik at NIST and the XSW measurements were carried out at X24A.

The MBE samples were grown on AXT SI GaAs (001) nominally-exact substrates which were chemically cleaned and then etched using a conventional $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ -deionized H_2O solution. After desorbing the surface oxide layer in the MBE chamber at 580°C in the presence of an As flux, a GaAs buffer layer, $0.5\ \mu\text{m}$ thick, was grown using conventional solid sources of Ga and As with effusion cell technology. Throughout the MBE growth the substrates were rotated at a rate of 8 rpm.

In a similar fashion to that described elsewhere [2, 3], 1 and $1/2$ ML samples were grown using a "temperature ramp" technique. During the buffer layer growth the temperature was linearly ramped to 480°C and the growth was interrupted for 3 sec with the As shutter open before the growth of the InAs layer. The GaAs and InAs growth rates were determined by RHEED oscillations to be 1.059 sec/ML and 5.04 sec/ML in reference samples with no substrate rotation. The InAs layer growth

was followed by another 3 sec interruption, after which a 200 Å GaAs cap was deposited at 480 °C. An additional series of samples were grown in which the buffer, 1 ML InAs and 200 Å GaAs cap layers were grown at a fixed temperature of 430, 480, 530 or 580 °C. The XSW results for both types of samples are shown in Figures 7.2 and 7.3. Note that the reflectivity curves, arising from Bragg reflection in the substrate crystals, are essentially identical for all samples. Thus a single experimental reflectivity curve is shown in each plot as a reference.

Description	P^H	F^H	In-As planar distance (Å)
1 ML (MBE) [1]	1.17 ± 0.02	0.58 ± 0.07	1.65 ± 0.03
1 ML (MBE) [2, 3]	1.16 ± 0.02	0.73 ± 0.1	1.64 ± 0.03
1 ML (MBE) [4]	1.154 ± 0.01	0.43 ± 0.03	1.63 ± 0.01
1 ML $\text{In}_{0.48}\text{Ga}_{0.52}\text{As}$ (MBE) [3]	1.053 ± 0.02	0.53 ± 0.1	1.49 ± 0.03

Table 7.1: XSW results reported from MBE-grown InAs and $\text{In}_x\text{Ga}_{1-x}\text{As}$ films in GaAs(001), with references indicated. The In-As planar distances were calculated from the measured coherent positions.

Results of previous XSW measurements for these types of samples are summarized in Table 7.1. Recall that the MET predicts the position of the In atoms to be $P^H = 1.1496$, relative to the GaAs (004)-planes. Our 1 ML sample grown by the temperature ramp technique (Figure 7.2) should be similar to the sample which was measured using back-reflection XSW [2, 3] and conventional XSW at 6 keV [4]. The samples were prepared in the same MBE chamber under similar conditions, although the previous sample was deposited on a stationary substrate with simultaneous RHEED measurements. Also, the previous sample had only a 25 Å GaAs cap, and the slower InAs growth rate of 23.5 sec/ML. These latter differences are not expected to change the sample quality. The sample rotation may be important, however, because the growth rates determined by RHEED during stationary MBE growth are almost certainly different from the growth rates obtained with a rotating substrate. It is possible that higher InAs growth rates in the rotating case could result in a degradation of the InAs layer quality if the InAs layer thickness exceeds 1 ML. In samples containing 2 and 4 ML of InAs, Woicik *et al.* [3] found that the coherent position is larger for samples with more InAs, which rules out this possibility. Alternatively,

Figure 7.2: Photon energy dependence of the reflectivity (bottom curve) and the In-L fluorescence yield near the GaAs(004) Bragg backreflection condition for 1 and 1/2 ML InAs samples grown by MBE using the temperature ramp technique. The solid lines are the best fits to the data points and the curves were offset for clarity.

Figure 7.3: Photon energy dependence of the reflectivity (bottom curve) and the In-L fluorescence yield near the GaAs(004) Bragg backreflection condition for a series of 1 ML InAs samples grown by MBE, with growth temperatures as indicated. The solid lines are the best fits to the data points and the curves were offset for clarity.

lower InAs growth rates would result in the incorporation of less than one complete ML of material. Referring to Figure 7.2 and Table 7.1 it appears that the 1 ML temperature ramp sample is not as highly strained as the previous sample, according to the lower value of P^H . This would be consistent with less than one complete ML of In atoms. At the same time the relatively high value of F^H suggests good InAs layer quality, comparable to the earlier sample. The value of P^H obtained for the 1/2 ML sample is comparable to the value for the $\text{In}_x\text{Ga}_{1-x}\text{As}$ layer studied in Reference [3], while F^H for the present sample is significantly higher.

In order to predict the XSW coherent position for a sample with less than 1 ML of InAs, we use the MET. For In atoms occupying random sites in a thin $\text{In}_x\text{Ga}_{1-x}\text{As}$ layer, Vegard's law gives the unstrained lattice constant of the layer, a_f , as

$$a_f = xa_{\text{InAs}} + (1-x)a_{\text{GaAs}} \quad . \quad (7.8)$$

The elastic constants for the alloyed layer are given by the concentration-weighted values for InAs and GaAs [53], as

$$\begin{aligned} C_{11}^f &= xC_{11}^{\text{InAs}} + (1-x)C_{11}^{\text{GaAs}} \quad , \\ C_{12}^f &= xC_{12}^{\text{InAs}} + (1-x)C_{12}^{\text{GaAs}} \quad . \end{aligned} \quad (7.9)$$

From MET

$$a_{\perp} = a_f(\epsilon_{\perp} + 1) \quad . \quad (7.10)$$

or

$$a_{\perp} = a_f - 2 \left[\frac{x C_{12}^{\text{InAs}} + (1-x) C_{12}^{\text{GaAs}}}{x C_{11}^{\text{InAs}} + (1-x) C_{11}^{\text{GaAs}}} \right] (a_{\text{GaAs}} - a_f) \quad . \quad (7.11)$$

If the In concentration, x , is known then P^H is determined from $P^H = a_{\perp}/a_{\text{GaAs}}$. Otherwise, from an experimentally measured P^H the value of x can be determined by substituting equation 7.8 into equation 7.11, and using the XSW result $a_{\perp} = P^H a_{\text{GaAs}}$. For the samples measured in the present study, the corresponding values of x are shown in Table 7.2. When this approach is applied to the results of Woicik *et al.* [3], in which XSW measurements were made for a single $\text{In}_x\text{Ga}_{1-x}\text{As}$ layer (nominally $x=0.48$), it is found that the measured $P^H=1.053\pm0.02$ is indicative of an alloy composition $x=0.38\pm0.14$. This is quite reasonable, since the input Ga:In ratio and growth rates were determined from growths with much thicker layers.

It is apparent from Table 7.2 that these MBE-grown samples do not contain complete In atomic planes residing in well-defined positions. The low value of P^H for the 1 ML temperature ramp sample might be explained by an InAs growth rate of only 69% of that required to deposit a complete ML. For the 1/2 ML the corresponding value is 54%.

Description	P^H	F^H	x
1 ML (temperature ramp)	1.10 ± 0.01	0.66 ± 0.05	0.69 ± 0.07
1/2 ML (temperature ramp)	1.04 ± 0.02	0.79 ± 0.08	0.27 ± 0.14
1 ML (430°C)	1.09 ± 0.03	0.71 ± 0.10	0.62 ± 0.21
1 ML (480°C)	1.09 ± 0.03	0.48 ± 0.09	0.62 ± 0.21
1 ML (530°C)	1.11 ± 0.04	0.68 ± 0.15	0.75 ± 0.27
1 ML (580°C)	1.03 ± 0.03	0.37 ± 0.06	0.21 ± 0.21

Table 7.2: XSW results and the In concentration, x , determined from experimentally measured values of P^H for MBE-grown InAs and $\text{In}_x\text{Ga}_{1-x}\text{As}$ films in GaAs(001).

The lack of any clear T_g -dependence is due to the competing temperature requirements for growth of the different layers in each sample. Higher temperatures are most suitable for producing smooth, uniform GaAs buffer layers, but are the least suitable for minimizing In segregation, according to the discussion of Section 5.2. Conversely, lower temperatures reduce the efficiency of the In/Ga exchange during the GaAs cap layer growth but result in poor buffer layer quality. This suggests that high-quality GaAs buffer layers must be carefully prepared and then suitable temperatures should be selected for the InAs layer and cap layer growth to produce good material. The following sections will describe the sample preparation and XSW results for ALE films.

7.3 XSW Study of ALE-Grown Films: I

In order to study the relationship between the measured XSW structural parameters and the PL optical parameters, InAs SQW samples were first produced by "ALE" using a growth sequence which had previously resulted in good PL emission from samples with several InAs coverages [5]. For this study the samples were grown at 50

Torr on SI VGF GaAs(001) epi-ready substrates, used with no additional cleaning. Following annealing under TBAs at 580 °C for 300 sec, a GaAs buffer layer of thickness 0.625 μm was grown by conventional MOVPE using TEGa and TBAs. ALE growth was performed at 390 °C. GaAs barrier layers (of thickness ~ 1.3 ML) above and below the InAs layer were grown by ALE in four 4-step cycles each consisting of a 3 sec H_2 purge, 8 sec of TMGa, another 3 sec H_2 purge, and finally 6 sec of TBAs. The InAs layer was deposited in a single cycle as above, with a 3 sec or 1.5 sec TMIn pulse, for the single and half MLs, respectively. The InAs growth rate was based on XRD thickness measurements of InAs homoepitaxial films deposited by ALE. After the top GaAs ALE layer, the temperature was raised to 500 °C and a thicker MOVPE GaAs layer was deposited using TEGa and TBAs. It should be emphasized that the GaAs "ALE" sequences were not optimized to produce exactly 1 ML/cycle.

In this study three samples were produced. For the XRD and XSW measurements, two samples were grown with nominal In depositions of 1 ML and 1/2 ML, and GaAs caps (ALE+MOVPE) of approximately 100 Å. Actual cap thicknesses were determined by XRD, as will be discussed. A third sample was grown for PL characterization with 1 ML of InAs and a total GaAs cap thickness of 2550 ± 25 Å, also determined by XRD. During each growth the sample surface was monitored by RDS.

The XSW results are shown in Figure 7.4. Comparing the 1 ML results with the MBE results reported previously, it appears that the ALE sample is not as highly strained. The coherent fraction of 0.77 ± 0.05 is among the best measured, but still lower than the Debye-Waller factor. For the half ML sample the F^H -value of 0.88 ± 0.12 corresponds to about 0.98 after accounting for the thermal effects.

Figure 7.5 shows a 4.2 K PL spectrum for the nominally 1 ML sample with the thicker GaAs cap. The peak location (1.459 eV) is close to the expected position for excitonic emission from an InAs ML in GaAs (Table 5.2), while the linewidth of 5.74 ± 0.01 meV is as narrow as the best results reported elsewhere and is indicative of satisfactory growth conditions. This spectrum was obtained using a double-grating 0.85 m spectrometer and GaAs photocathode photomultiplier tube, rather than the Bomem system.

Figure 7.4: Photon energy dependence of the reflectivity (bottom curve) and the In-L fluorescence yield near the GaAs(004) Bragg backreflection condition for 1 and 1/2 ML InAs samples grown by ALE. The solid lines are the best fits to the data points and the curves were offset for clarity.

Figure 7.5: PL emission from a nominally 1 ML InAs film on GaAs(001), buried beneath a 2550 ± 25 Å GaAs cap.

What is the significance of the XSW positional measurements? Previous measurements of MBE samples support the macroscopic description of this interface [1]-[3]. Our results may be used to predict the layer composition in a similar fashion to the XRD determination of alloy concentration by the measurement of lattice constant in thicker films [136].

Assume that the XSW position is correct, and that the In atoms are arranged in a single layer. Based on the experimental result this layer cannot be completely covered by In. If the layer actually consists of an alloyed distribution, $\text{In}_x\text{Ga}_{1-x}\text{As}$, then x can be found from the MET using the method of Section 7.2. The measured values of $a_{\perp} = 6.31 \pm 0.06$ Å and $a_{\perp} = 6.01 \pm 0.12$ Å lead to $x = 0.79 \pm 0.07$ and

$x = 0.45 \pm 0.15$, for the 1 ML and 1/2 ML films, respectively. For the MBE half-ML samples discussed previously the alloyed distribution of cations is to be expected because the In and Ga shutters were open simultaneously during the MBE growth. In contrast, for the ALE films no Ga-source molecules were incident on the substrate during the InAs layer growth.

Figure 7.6 shows the XRD data for the 1 ML and 1/2 ML samples. It is interesting to note that the Pendellösung fringes are clearly visible out to 7200 arcsec on either side of the main substrate reflection. This is somewhat remarkable for such thin layers of InAs capped by nominally 100 Å of GaAs. In HRXRD studies of thin InAs layers reported previously [1, 13], the GaAs caps typically exceeded ~ 275 Å.

The XRD data were modeled using the RADS software (Section 3.3). The NSW data discussion has suggested that the In atoms reside in single $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers, and that the group III layer has a distance $a_\perp/4$ from the last As plane of the substrate. Thus the net GaAs cap $\rightarrow$ substrate displacement is $a_\perp/2$.

Figure 7.6 shows the results of simulations with these alloy compositions and layer thicknesses. In addition, the GaAs cap thicknesses determined from the simulations are 97 ± 3 Å for the 1 ML sample, and 85 ± 3 Å for the 1/2 ML sample. Comparing the data and the simulations, it appears that layer properties inferred from the NSW results provide a good description of the XRD data. It is important to mention that the XRD data could be interpreted differently. For instance, a reasonable simulation for the 1 ML sample rocking curve could have been obtained by supposing a single InAs layer and an associated cap $\rightarrow$ substrate displacement of approximately 3.0 ± 0.3 Å, although this can not be related to a physical distribution of In atoms.

Two factors may contribute to the apparently incomplete coverage in the ML sample. Without the benefit of RHEED growth oscillations, the ALE process is at a disadvantage compared with MBE. Specifically, the In pulse times were based on InAs bulk growth rates and we rely upon *ex-situ* XRD characterization to estimate the amount of In deposited. The In coverage can not be determined sufficiently precisely to distinguish between a full ML and a 79% alloy layer with this method. Secondly, the growth process employed the flash-off technique (Section 5.2). Raising the growth temperature after the GaAs cap ALE cycles may result in a greater-than-intended

Figure 7.6: X-Ray rocking curve data obtained near the GaAs(004) symmetric substrate reflection, for $\Delta\theta = \theta - \theta_B$. Data for the 1 and 1/2 ML samples (upper and lower curves, respectively) are indicated by points. Solid lines indicate the results of RADS simulations as described in the text.

desorption of segregated In atoms, thus contributing to the lower In coverage.

This interpretation of an alloyed distribution of In atoms, particularly in the 1/2 ML case, suggests that for subML coverages the In atoms do not form ML islands, as proposed in the past [13, 119, 121]. Ideally, such islands would reside at the ideally-strained InAs position (1.6247 Å), although edge effects at InAs islands might lower the measured position. We must emphasize that this interpretation is not unique and unambiguous. In segregation could be involved, although calculations suggest that segregation alone cannot explain the low values of P^H measured in these samples. The calculations will be discussed in Section 7.6.4. The next section will describe experiments aimed at studying the effect of growth conditions on In segregation in ALE.

7.4 RDS Study of ALE Heteroepitaxy

The RDS transient signal monitored at the As-dimer energy (2.6 eV) is quite sensitive to the presence and orientation of As dimers along the surface of a GaAs(001) crystal. To extend the study published by Arès which clearly showed In segregation during ALE growth of GaAs/InAs/GaAs heterostructures [90], attempts were made to reduce or eliminate the segregation by suitable modifications in the growth parameters.

The ALE growth sequence described in Section 7.3, although clearly suitable for producing material with good PL emission, does not make use of true “atomic layer” conditions. In the following the method for establishing the ALE 1 ML/cycle conditions for GaAs growth will be described. The temperature dependence of In segregation was explored for growth temperatures between 400 and 500 °C.

The sample preparation began by annealing each sample under TBAs for 5 min at 580 °C, followed by the MOVPE growth of a ~ 1450 Å GaAs buffer at 580 °C using TEGa and TBAs with flow rates of 8.07 $\mu\text{mol/min}$ and 198 $\mu\text{mol/min}$, respectively. All samples were grown on AXT SI GaAs(001) VGF epi-ready substrates with no additional cleaning. ALE growth was performed with TMGa at 25.7 $\mu\text{mol/min}$, TMIn at 1.65 $\mu\text{mol/min}$ and TBAs at 48.5 $\mu\text{mol/min}$. The total reactor flows and gas velocities for ALE and MOVPE were given in Table 6.1.

Figure 7.7: RDS transient signal during three consecutive GaAs ALE cycles at 400 °C. The dashed, vertical line marks the signal level after 10 sec of TMGa. The data were offset for clarity.

To determine the alkyl pulse durations required to produce 1 ML/cycle at different temperatures, a single substrate crystal was used. For temperatures greater than 400 °C the ALE sequence: 10 sec H_2 ||7 sec TMGa||10 sec H_2 ||7 sec TBAs was repeated three times, while monitoring the 2.6 eV RDS transient. At 400 °C, 12 sec of TMGa and TBAs were used because of the slower growth and decomposition rates at this temperature. Figure 7.7 shows the RDS transients for the three ALE cycles at 400 °C, which are clearly reproducible from cycle-to-cycle. During the TMGa pulse the RDS signal saturates after an initial abrupt change. This saturation reflects the self-limiting nature of the growth and corresponds to a 1 ML Ga surface coverage.

From similar RDS signals observed at the other temperatures it was possible to determine the TMGa pulse lengths required to produce 1 ML of GaAs. The durations of the H₂ and TBAs pulses are less critical. The H₂ pulse is used mainly to separate the group III and group V pulses in time. The TBAs pulse must be sufficient to provide 1 ML of As coverage, but excess As-adsorption does not increase the amount of GaAs deposited [16].

At higher T_g the TMGa saturation was less well-defined because the ALE process was no longer self-limiting. In these cases the saturation time was estimated from the RDS transients and confirmed by growing samples with 1 ML of InAs capped by 200 GaAs ALE cycles. HRXRD determinations of the cap thicknesses were used to ensure that the growth sequences produced close to 1 ML/cycle. The ALE sequences used for the remainder of this study consisted of: 2 sec H₂|| t sec TMGa||2 sec H₂||6 sec TBAs. Here t is the TMGa pulse time according to Table 7.3. The InAs cycle used a 3 sec TMIn pulse.

Growth Temperature (°C)	TMGa Pulse Time, t (sec)
400	10
420	6
440	3.5
460	2
480	1.6
500	1

Table 7.3: TMGa pulse times required for 1 ML/cycle ALE growth at different temperatures.

After establishing the appropriate TMGa durations, samples were produced at temperatures between 400 and 500 °C. Each consisted of a GaAs buffer layer, 10 GaAs ALE cycles, 1 InAs ALE cycle, 35 GaAs ALE cycles, and finally ~2900 Å of GaAs grown by conventional MOVPE using the buffer layer growth parameters. The additional cap layer was added to allow PL measurements. Throughout each sample growth the RDS transient was monitored at 2.6 eV. Unfortunately, the PL spectra for this series of samples were dominated by recombination at carbon impurities, preventing the observation of In excitonic emission. Apparently the amount of carbon

incorporated in the 46 ALE cycles is excessive. This illustrates a major shortcoming of the ALE technique.

A phenomenological analysis of the RDS data was performed in the following way. For each cycle, it is reasonable to assume that the most stable surface during the cycle will be achieved at the end of the last step, the TBAs pulse. To quantitatively study the transient signal, the points in each RDS transient corresponding to the end-of-cycle signal level were isolated. This allowed an examination of the transient signal as a function of the number of layers deposited, rather than as a function of time. This alleviates the complication that ALE cycles for different temperatures have different durations, as required for 1 ML/sec GaAs growth. An RDS spectrum obtained in this way is shown in Figure 7.8.

For the temperatures considered here, the RDS signal prior to the InAs cycle was highly reproducible from cycle-to-cycle and the end-of-cycle levels were essentially constant during the GaAs ALE. Immediately following the InAs cycle, the RDS signal underwent a dramatic change in intensity and the end-of-cycle data followed a sigmoidal relaxation back to the original intensity. In Figure 7.9 the end-of-cycle data for samples grown with 1 ML GaAs ALE cycles at different temperatures are presented.

The solid lines in this figure are the results of least-squares-fitting the data to a purely empirical expression with a Boltzmann form

$$I(n) = \left[1 + \exp \left(\frac{n - n_0}{\mathcal{N}} \right) \right]^{-1} . \quad (7.12)$$

Here $I(n)$ refers to the normalized RDS signal as a function of the number of GaAs cap cycles deposited, n . The quantity n_0 is related to the half-width of the relaxation, while $\mathcal{N}$ is related to the decay rate of the segregation process.

The fits to the data using this expression appear quite good. The RDS half-widths decrease smoothly with decreasing growth temperature as shown in Figure 7.10 and may saturate at a minimum near 400 °C. A more extensive study would be necessary to clarify the temperature dependence of these parameters. The most important observation is that using these ALE sequences, there remains considerable In segregation even at 400 °C.

Figure 7.8: RDS transient signal during the deposition of 10 GaAs ALE cycles; 1 InAs cycle; and 35 GaAs capping cycles at 460 °C. The empty circles indicate the position of the signal at the end of each complete cycle.

Based on the discussion of Section 5.2, the relaxation would be expected to decay exponentially, according to Equation 5.7. The In surface concentration after n capping layers, x_n , in this equation follows the form

$$x_n = (1 - \sigma)\sigma^{n-1} = (1 - \sigma)e^{(n-1)\ln\sigma} \quad , \quad (7.13)$$

where σ is the segregation coefficient. The sigmoidal shape may indicate a more complicated process. Also, the RDS end-of-cycle level is not necessarily a linear function of the In surface concentration so the connection with Equation 7.13 may not be transparent.

Efforts were made to reduce the In segregation by adjusting the TMGa pulse times

Figure 7.9: Temperature dependence of the RDS end-of-cycle transients during the deposition of 35 GaAs capping layers by ALE. The solid lines indicate the fits using the Boltzmann expression. The curves were normalized and offset for clarity.

Figure 7.10: Temperature dependence of the RDS end-of-cycle fit parameters from the Boltzmann model. The solid lines are guides for the eye.

Figure 7.11: TMGa pulse time dependence of the RDS end-of-cycle transients during the deposition of 35 GaAs capping layers by ALE. The solid lines indicate the fits using the Boltzmann model. The curves were normalized and offset for clarity. The values in parentheses indicate the growth rates as determined by *ex-situ* XRD.

at 400 °C. The results are shown in Figure 7.11. At first glance it appears that the segregation is slightly reduced with the longest TMGa pulses. The amount of GaAs deposited per cycle is slightly different in each case, however, and so the segregation is not changed significantly as the TMGa pulse length is changed. Section 5.2 suggests that the ALE process is unsuitable for producing abrupt interfaces and this is verified by these experiments. The lack of As overpressure during the cap growth allows In segregation regardless of the temperature or TMGa pulse duration. The TMGa flow rate could play a role, but this was not pursued. The next section discusses the XSW results obtained for a SQW structure grown by ALE using the methods described in this section.

7.5 XSW Study of ALE-Grown Films: II

To compare the XSW results of Section 7.3 with the case of an ALE sample with true 1 ML/cycle GaAs growth, an ALE sample was produced at 400 °C using the sequence: 2 sec H₂||10 sec TMGa||2 sec H₂||6 sec TBAs for GaAs growth. For InAs growth a 3 sec TMIn pulse was used. Figure 7.12 shows the XSW data and the fitting results. For this sample also, P^H has a lower value than expected for a perfect InAs layer ($P^H=1.1496$) and F^H is slightly lower than for the 1 ML sample shown in Figure 7.4. Using the method of Section 7.2, the data are consistent with In atoms arranged in a single In_{*x*}Ga_{1-*x*}As layer with $x=0.89\pm0.14$. While this interpretation of the data is possible, it neglects the In segregation directly observed using RDS. As mentioned earlier, calculations accounting for the segregation process cannot adequately describe these data. Details of the calculations will be discussed in Section 7.6.4. At any rate, the ALE process is not expected to be the most suitable method for producing sharp InAs distributions. The next section involves the study of InAs films in GaAs grown by conventional MOVPE, which forms the bulk of this thesis.

Figure 7.12: Photon energy dependence of the reflectivity (bottom curve) and the In-L fluorescence yield near the GaAs(004) Bragg backreflection condition for a 1 ML InAs sample grown by ALE at 400 °C. The solid lines are the best fits to the data points.

7.6 InAs QWs in GaAs(001) Grown by MOVPE

This section describes the growth and characterization of the main group of samples studied in this thesis. First, RDS was used to perform a pseudo-real-time investigation of the GaAs/InAs/GaAs growth sequence using SL structures. Samples produced using single cycles of this sequence were then studied by XSW, XAFS and XRD. Additionally, a group of similar samples was examined by PL spectroscopy.

7.6.1 MOVPE Growth and In-situ Characterization

This series of samples was grown at 50 Torr using TBAs, TEGa, and TMIn with flow rates of 198, 8.07, and 1.98 $\mu\text{mol/min}$, respectively. All samples were grown on AXT SI GaAs(001) VGF epi-ready substrates with no additional cleaning. In all cases the substrates were annealed at 580 $^{\circ}\text{C}$ under TBAs, followed by the growth of a 1450 $\text{\AA}$ GaAs buffer layer using TEGa and TBAs (hereafter called a standard buffer). AFM images of buffer layers grown in this way revealed excellent morphologies, with clear evidence of step-flow growth and terraces about 0.1 μm wide, as shown in Figure 7.13.

Samples were produced at temperatures between 450 and 600 $^{\circ}\text{C}$. For the multi-transient spectroscopy of the InAs QW growth, each sample was allowed to equilibrate at the growth temperature, T_g , under TBAs. The growth sequence for the SL structure was then initiated. Each cycle consisted of a 20 sec pause under TBAs; 3 sec of InAs growth; a second TBAs pause; and 100 $\text{\AA}$ of GaAs growth. The GaAs growth rates determined by HRXRD are given in Table 7.4. Here the growth rates were determined by growing a GaAs buffer layer, and then depositing 1 ML of InAs and a reasonably thick (~ 2000 $\text{\AA}$) GaAs cap layer at T_g . HRXRD data for calibration samples produced in this way were evaluated using the RADS software to estimate the GaAs cap thickness and hence the growth rate, based on the cap growth duration.

The 2.6 eV RDS transient signal was initially studied during the growth of 10 SL periods with a sampling frequency of 8 Hz. During these cycles the RDS signal followed an oscillatory envelope, similar to the Fabry-Pérot behaviour reported by Koch *et al.* [105]. After these ten cycles the signal stabilized enough to commence the

Figure 7.13: AFM topography image for a GaAs reference buffer layer.

multitransient measurements.

Time-resolved energy spectra were constructed by recording the transient RDS signal at a single energy for individual periods of the SL growth [101]. Measurements were made from 1.5 eV to 4.9 eV in increments of 0.2 eV with each transient synchronized to the same instant of the exposure cycle. These data were then reorganized to form 400 18-point spectra at 0.125 sec increments. After these 18 cycles, the transient signal at 2.6 eV was monitored during the growth of 7 additional SL periods to ensure the reproducibility of the first 10 cycles, without oscillations.

For these SLs, with total thicknesses of ~ 3600 Å, the accumulated strain caused by the lattice mismatch of InAs and GaAs ($\sim 7\%$) results in misfit dislocation formation in the films. This effect manifests itself as a cross-hatched surface morphology observed using AFM. Notwithstanding, the RDS spectra, characteristic of the local

Temperature (°C)	Growth Rate (Å/sec)
450	6.88±0.06
500	7.28±0.06
550	7.56±0.06
600	7.44±0.06

Table 7.4: MOVPE growth rates used in SL sample preparation for *in-situ* RDS study.

dimer arrangements, were unaffected by this long-range effect. AFM images of the SL structures are presented in Figure 7.14. Note the very straight, well-defined lines in the cross-hatching and the perfect 90° intersections.

Figure 7.15 shows RDS energy spectra at several temperatures, obtained for the GaAs surface held under TBAs, and during GaAs growth. All data presented here show the real part of the RDS.

$$\frac{\Delta r}{r} = 2R\epsilon \left[\frac{\tilde{r}_{110} - \tilde{r}_{\bar{1}\bar{1}0}}{\tilde{r}_{110} + \tilde{r}_{\bar{1}\bar{1}0}} \right] . \quad (7.14)$$

which is primarily related to the imaginary part of the dielectric function [96]. These data may be interpreted using the “RDS database” described in Section 5.3 [97]. At all temperatures the GaAs surface under TBAs corresponds to the d(4×4) reconstruction, distinguished by the negative feature near 2.6 eV due to As dimers along the [110]-axis [99], and the peak near 4.0 eV. Two or more outer layers of As terminate this surface. While the spectra under TBAs are temperature-independent, this is not the case for the GaAs growing surfaces. At 400 °C the spectrum exhibits weakly positive features near 2.6 eV and 4.2 eV, and a negative dip near 2.1 eV. This indicates the presence of both As and Ga dimers on the surface, presumably due to incomplete cracking of TBAs at lower temperatures. The spectrum may be associated with a (1×6)-like reconstruction [98]. With increasing T_g the spectra show a trend towards the d(4×4)-like signature. At 600 °C the growing surface is indistinguishable from the surface held under TBAs.

A series of samples was grown, each consisting of one SL period, to study the T_g -dependence of the 2.6 eV RDS transient response as shown in Figure 7.16. The principle illustrated in Figure 7.15 is similarly evident in these data; the RDS signal

Figure 7.14: AFM topography images for SL structures described in the text. The samples were prepared at temperatures: a) 450 °C, b) 500 °C, c) 550 °C and d) 600 °C.

shows a distinct change when the GaAs growth is initiated, an effect which is reduced at higher T_g . When the TEGa flow is discontinued and the surface is held under TBAs, the signal decays back to the TBAs-surface level, with a rate constant exhibiting a strong T_g -dependence. For the sample at 400 °C the signal does not completely recover during the 20 sec TBAs pause, while the transient for the 600 °C sample drops to its original level almost instantly. This behavior is likely related to the TBAs molecular decomposition, which is complete above about 475 °C. The decay time is thus representative of the time required to form an excess layer of As on the

Figure 7.15: Temperature dependence of the RDS signal ($\Delta r/r$) for GaAs surfaces under TBAs (solid lines) and during GaAs growth (dashed lines). The spectra were corrected for zero offsets using spectra obtained with the susceptor rotated 90°.

surface.

Figure 7.16: 2.6 eV RDS transients during single SL cycles, with temperatures as noted. The transients were normalized and offset by arbitrary amounts to permit clear comparisons. The zero of time corresponds to the onset of the TMIn flow.

At all temperatures the RDS signal increases abruptly when the TMIn flow begins. The signal exhibits a “peak overshoot” at the lowest temperatures, where the signal increases steadily to its maximum value and then decreases gradually until the TMIn flow is terminated. This effect becomes less pronounced at higher temperatures and is no longer evident above 450 °C. This behavior is similar to that reported for heteroepitaxy of ternary and quaternary materials [105].

Following a 20 sec TBAs purge of the InAs-on-GaAs surface, which stabilizes the signal level, the RDS signal at all temperatures increases abruptly when the TEGa flow is initiated, rises to a maximum and then decays. In this case the transient peak is observed at all temperatures. Using similar samples with much thicker GaAs cap growths we have established that this signal actually exhibits a weak, damped

oscillation behavior [105] with a period of the order of 1 minute. This effect is not apparent in the short 100 Å GaAs growth for the samples of Figure 7.16.

Figure 7.17 shows the 2.6 eV RDS transient recorded during the growth of the first 10 SL periods at 500 °C. Consecutive cycles are quite reproducible and exhibit the features observed in Figure 7.16. In addition, the series of cycles follows a very slight damped oscillatory envelope which dies out during these 10 cycles. Subsequent cycles are highly reproducible with no oscillations.

Figure 7.17: 2.6 eV RDS transients for the first 10 periods of the SL growth at 500 °C. These cycles allowed the signal to stabilize before the acquisition of the multitransient spectra.

After these 10 stabilization cycles the full time-resolved RDS energy spectra were collected. Figures 7.18 and 7.19 each contain a series of such spectra corresponding to different stages of the growth of a single SL period, at growth temperatures of 450 °C and 600 °C, respectively. For the sample at 450 °C the first spectrum (Figure 7.18(a)) depicts the GaAs surface under TBAs similar to Figure 7.15. When the InAs growth is

Figure 7.18: Multitransient energy spectra representing the development of surface anisotropies for the growth of a single SL period at 450 °C. These spectra correspond to (a) GaAs after 20 sec TBAs pause; (b)-(d) 1, 2 and 3 sec of InAs growth; (e) after 20 sec TBAs pause; (f)-(j) 1, 3, 5, 7 and 9 sec of GaAs cap growth. Consecutive spectra were offset from one another for clarity. The short, horizontal lines indicate zero levels.

Figure 7.19: Multitransient energy spectra representing the development of surface anisotropies for the growth of a single SL period at 450 °C. These spectra correspond to (a) GaAs after 20 sec TBAs pause; (b)-(d) 1, 2 and 3 sec of InAs growth; (e) after 20 sec TBAs pause; (f)-(j) 1, 2, 3, 5, and 6 sec of GaAs cap growth. Consecutive spectra were offset from one another for clarity. The short, horizontal lines indicate zero levels.

initiated the RDS minimum moves rapidly to near 1.7 eV (Figure 7.18(b)-(d)). The negative feature of the TBAs-ambient surface at 2.5 eV becomes positive with the impinging TMIn molecules. A local minimum develops in the spectrum near 2.9 eV, while the maximum near 3.9 eV remains similar to the feature observed for the TBAs-ambient surface. These spectral characteristics observed during InAs growth agree very well with those reported by Zorn *et al.* [107] which were identified by low energy electron diffraction as arising from a (2×4) -like InAs reconstruction. The surface evolution during InAs growth has many similarities to that observed by Scholz *et al.* in MBE [137], although it should be emphasized that our data are representative of the growing surface *without* interruptions.

The InAs-on-GaAs surface is essentially unchanged during the following 20 sec under TBAs (Figure 7.18(e)). When the GaAs growth is initiated (Figure 7.18(f)) the 2.5 eV feature increases very rapidly, accounting for the peak behaviour noted in Figure 7.16. The origin of this strong anisotropy is not clear at present. Within approximately 3 sec (Figure 7.18(g)) the spectrum reaches the steady-state characteristic of 450 °C GaAs growth, the (1×6) -like spectrum identified in Figure 7.15. It is noteworthy that during InAs growth the RDS spectrum reaches a stable (2×4) -like InAs spectrum during the growth of only 1 ML, but for GaAs cap growth the 3 sec required for the signal to stabilize represents approximately 20 Å (7 ML) of material. This may be related to In segregation, as observed during ALE growth [90], although the effect can not be clearly inferred from the data.

It is tempting to suppose that during the cap growth the total RDS spectrum, $(\Delta r/r)$, consists of a linear combination of the InAs, $(\Delta r/r)_{\text{InAs}}$, and GaAs, $(\Delta r/r)_{\text{GaAs}}$, spectra, i.e. $(\Delta r/r) = y(\Delta r/r)_{\text{InAs}} + (1 - y)(\Delta r/r)_{\text{GaAs}}$, where y is the fraction of In on the surface. Attempts to model the data in this way were prohibited by the strong peak overshoot occurring at the beginning of the cap layer growth.

At higher T_g many of the preceeding features are also observed. One main difference, visible in Figure 7.19, is that the spectra obtained during the GaAs cap growth (Figure 7.19(f)-(j)) quickly recover to the $d(4 \times 4)$ -like lineshape, as opposed to the (1×6) -like GaAs spectrum observed at lower T_g . This is consistent with the spectrum

for the GaAs growing surface shown in Figure 7.15 and is related to the higher effective As-partial pressure under these conditions. In addition, evidence of the In-related feature at 2.5 eV persists for longer than 3 sec following GaAs capping, corresponding to almost 8 ML of growth.

XRD results from the SL structures are shown in Figure 7.20. Comparing the experimental curves with RADS simulations (Section 3.3) for an ideal SL (35 periods of 1 ML InAs/100 Å GaAs), it is found that the SL satellite features are reasonably narrow, but slightly broader than for the ideal structure. This broadening is due to the presence of misfit dislocations in the crystal corresponding to the cross-hatched patterns in Figure 7.14.

7.6.2 XSW Study of MOVPE-Grown Films

The SL structures and the RDS characterization presented in the preceding section were used to gain an understanding of the InAs/GaAs heteroepitaxial growth mechanisms, and the T_g -dependence of these processes. The goal of this was to provide a basis for understanding the structural details of the buried InAs 1 ML and 1/2 ML SQWs which will now be discussed. In the following the main experimental results of this thesis will be presented. The section will begin with a description of the sample preparation and will then present the results of XRD, XSW, XAFS and PL studies.

Epitaxy was performed at 50 Torr using SI VGF GaAs(001) epi-ready substrates with no additional cleaning, beginning with the growth of a standard buffer. Two series of samples were prepared for this study because of the conflicting requirements of the XSW and PL measurements. In the XSW case, the GaAs cap thicknesses must be sufficiently small to prevent interference effects (Pendellösung) between the diffracted beams from the substrate and the cap. A thickness of about 100 Å was appropriate for this. For PL measurements a thicker cap is required to prevent the reduction of the In-excitonic emission due to nonradiative recombination at the sample surface. A thickness of about 2000 Å is more than adequate for this purpose.

Following the buffer layer growth, each sample was allowed to equilibrate at the

Figure 7.20: XRD results for the SL structures as a function of angle near the GaAs(004) reflection. Data for samples grown at 450 °C, 500 °C, 550 °C and 600 °C are shown in ascending order and are offset by two decades for clarity. The top curve shows the simulation results for an ideal SL structure, as indicated.

desired growth temperature, T_g . GaAs barrier layers of thickness ~ 100 Å were deposited above and below the InAs layer (1 ML or 1/2 ML) which was also grown at T_g using TMIn at $1.98 \mu\text{mole/min}$ and TBAs at $198 \mu\text{mole/min}$, yielding a growth rate of approximately 1 ML per 3 s. For the PL samples an additional GaAs cap layer (~ 1900 Å) was deposited at 580°C .

7.6.3 X-Ray Diffraction

HRXRD data for 1 ML and 1/2 ML samples are shown in Figures 7.21 and 7.22. The experimental curves are compared to RADS simulations using a 3-layer model consisting of the GaAs substrate, a single In-containing layer, and a GaAs cap layer. For the 1 ML samples, the thickness of the strained InAs layers used in the simulations was 3.25 Å, as predicted by the MET [52], assuming single layers of In atoms and coherency of the InAs layers with the GaAs substrate. For the 1/2 ML samples the MET was also used, assuming single $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers, as will be discussed. From the interference fringes an accurate measurement of the GaAs cap thickness is obtained. However, this technique is slightly less sensitive to the distribution of In atoms in the SQW layer, particularly in the case of these sandwich structures with very thin GaAs caps. It was pointed out [1] that complementary information may be obtained by using XSW in addition to XRD.

7.6.4 XSW Analysis

Figures 7.23 and 7.24 show the XSW data for the 1 and 1/2 ML InAs samples prepared at several growth temperatures. MET [52] predicts that a single InAs ML in GaAs has $P^H = 1.146$ under pseudomorphic conditions [2]. Comparing the raw data of Figures 7.23 and 7.24 with Figure 7.1 it is clear that the In atoms do not occupy the same positions as the substrate Ga atoms. The best 1 ML sample, structurally, is the one with $T_g = 550^\circ\text{C}$, having an ideal P^H and the highest F^H . 1/2 ML samples grown at 400 and 600°C have similar P^H -values to one another and high values of F^H . Notice the more bulk-like characteristics of the 1/2 ML data, specifically the pronounced dip at the low-energy side of the Bragg reflection. Assuming that the

Figure 7.21: HRXRD results obtained near the GaAs(004) symmetric substrate reflection. The data for the 1 ML samples with several growth temperatures are indicated by points. Solid lines denote the results of dynamical simulations with the GaAs cap thicknesses indicated, as described in the text. The curves were offset for clarity.

Figure 7.22: HRXRD results obtained near the GaAs(004) symmetric substrate reflection. The data for the $\frac{1}{2}$ ML samples with several growth temperatures are indicated by points. Solid lines denote the results of dynamical simulations with the GaAs cap thicknesses indicated, as described in the text. The curves were offset for clarity.

1/2 MLs consist of single $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers and using the method of Section 7.2 the following values of x were found from the XSW results: 0.63 ± 0.14 , 0.56 ± 0.14 and 0.69 ± 0.14 , in order of increasing T_g .

To clarify the mechanism producing the higher-than-ideal coherent positions in the 1 ML samples with the lowest T_g -values, we consider the possibility of In atoms occupying multiple sites in the crystal. For In atoms occupying n positions (P_i^H) relative to the diffraction planes, Equations 3.54 and 3.55 give [32]

$$F^H = (G_H^c{}^2 + G_H^s{}^2)^{1/2} . \quad (7.15)$$

and

$$P^H = \frac{1}{2\pi} \tan^{-1} \left(\frac{G_H^s}{G_H^c} \right) + \begin{cases} 0.5 & \text{if } G_H^c < 0 \\ 0 & \text{otherwise} \end{cases} , \quad (7.16)$$

with G_H^c and G_H^s defined in Section 3.2.2

Previous XSW measurements [1] were interpreted assuming In surface segregation during the GaAs cap layer growth. Consider the possible results of an XSW measurement for a buried layer in GaAs(001) including this process, with 1 ML total In content. It is very important to note that a single XSW measurement provides only one Fourier component of the In distribution. This presents a uniqueness problem when one attempts to infer additional information in this way, although the measured values do place some constraints on the structural possibilities.

The issue of In segregation was discussed in Section 5.2. We consider two possibilities: (i) Each group III layer consists of an In.Ga alloy, with the composition of sequential layers graded in the growth direction. The composition of the n th layer, $\text{In}_{x_n}\text{Ga}_{1-x_n}\text{As}$, is $x_n = (1 - \sigma)\sigma^{n-1}$ from Equation 5.7 and the strained lattice constant of each layer is found from Equations 7.8-7.11. In this scenario the In atoms are located at 1/2 the lattice constant of the strained layer, which is a function of x_n . The other possibility is: (ii) Each group III layer contains In and Ga atoms as above, with the In atoms arranged in equidistant “terraces” or islands. For each layer the tetragonally distorted InAs cell is expanded 14.6% in the (001)-direction compared to GaAs. This is the scheme used in Ref [1]. The two models are illustrated in Figure 7.25.

Figure 7.23: Photon energy dependence of the reflectivity (bottom curve) and the In-L fluorescence yield near the GaAs(004) Bragg backreflection condition for a series of 1 ML InAs samples grown by MOVPE, with growth temperatures as indicated. The solid lines are the best fits to the data points and the curves were offset for clarity.

Figure 7.24: Photon energy dependence of the reflectivity (bottom curve) and the In-L fluorescence yield near the GaAs(004) Bragg backreflection condition for a series of 1/2 ML InAs samples grown by MOVPE, with growth temperatures as indicated. The solid lines are the best fits to the data points and the curves were offset for clarity.

It should be noted that (i) implicitly uses the VCA by assuming that both In and Ga atoms reside in the same cation plane. Mikkelsen and Boyce's study proved that the In-As and Ga-As bond lengths in the ternary alloy do not deviate significantly from their native values [54], and that the atoms do not occupy the VCA positions. Model (i) should be considered as a first approximation in lieu of a more complete description.

Figure 7.25: The distribution of In atoms relative to the GaAs(004) planes according to the two models described in the text. In model (i) the distance, $d_{\perp}^i$, between each cation plane and its corresponding As plane is a function of the In concentration, x_n . For model (ii) the spacing is the same for all planes, independent of In content.

Model (ii) assumes terracing of the In atoms, and neglects edge effects which are likely present at the boundaries between the InAs and the surrounding GaAs. Additionally, this assumes equal strain in all InAs layers in spite of the differences in In content. In this respect model (i) is somewhat more realistic.

The possible XSW parameters have been estimated using both models. In case (i), with a given σ , the lattice constant for the n th layer was estimated using Vegard's law and Equation 5.7 to give the bulk lattice constant. The effect of strain was included using MET as discussed previously. If the (004)-plane spacing between the i th In,Ga layer and the corresponding As-plane is denoted by $d_{\perp}^i$, then the total distance of the n th layer from the last As-plane of the substrate is

$$d^n = 2 \sum_{i=1}^{n-1} d_{\perp}^i + d_{\perp}^n . \quad (7.17)$$

These positions may then be substituted into Equations 3.56 and 3.57 from which F^H and P^H are determined.

The results for a range of segregation coefficients are shown in Figures 7.26 and 7.27 for the two cases. For model (i) in which the segregation produces a graded InGaAs alloy, the theoretical XSW parameters P^H and F^H are found to decrease with increasing segregation, but remain close to the values for the ideal ML. It is clear from the figures that only (ii) can explain the experimental results in which $P^H > 1.15$. For samples grown at 400°C and 500°C, the XSW coherent positions are found to be consistent with $\sigma=0.30$, and $\sigma=0.15$, respectively, as indicated. Moreover, the experimental values of F^H are consistent with this interpretation, if the Debye-Waller factor is included. Let us reemphasize that this interpretation of the XSW data is not entirely conclusive.

Comparing the data with the island model, the segregation coefficients inferred from the data are found to be *greater* for the samples grown at the lowest temperatures. Since Giannini *et al.* measured only one sample using XSW [1], the T_g -dependence was not discussed. They found $P^H = 1.17 \pm 0.02$, $F^H = 0.58 \pm 0.07$ which was related to a segregation coefficient of $\sigma \approx 0.25$ when the structure was grown by MBE with the flashoff technique. In their experiment, the InAs ML and the first 5 ML of the GaAs cap were deposited at 420 °C. The temperature was then raised to 540 °C to desorb the segregated In. Finally, 300 Å of GaAs were deposited at 540 °C.

Previous reports of In segregation in GaAs(001)/InAs/GaAs structures have used both thermodynamic and kinetic models to describe the process (Section 5.2). Several experiments [80]-[84] have found that In segregation increases with increasing

Figure 7.26: XSW parameters as a function of segregation coefficient, σ , predicted by model (i) described in the text, with 1 ML total In coverage.

Figure 7.27: XSW parameters as a function of segregation coefficient, σ , predicted by model (ii) described in the text. In the bottom half of the figure the experimental XSW coherent positions (small hollow squares) are compared with the values of the segregation coefficient, σ , which might produce the measured P^H . The solid and dashed rectangles are used to indicate the range of possible values of σ for the 1 ML samples grown at 400 and 500 °C, respectively. In the top half of the figure the corresponding values of F^H are indicated, as well as the experimental values.

T_g , ruling out the thermodynamic model. The kinetic model [85] reproduces the fixed-temperature results and accounts for the observed increase with growth temperature [92]. The incident As flux has also been shown to affect the segregation [93], and might be included in an even more complete model.

An interpretation of the XSW data using model (ii) would indicate increasing In segregation with decreasing T_g . This disagrees with the experimental evidence for MBE growth obtained by other means [80]-[84] due to differences in the growth conditions between MBE and MOVPE. The results for MBE-grown samples presented in Section 7.2 indicated that the growth temperature of the GaAs barriers also plays a pivotal role.

For the 1 ML samples grown at 550 °C and 600 °C the XSW results indicate near ideal In distributions, particularly in the former. This is attributed to the favourable conditions created in the MOVPE environment [79]. Consider the requirements for minimal segregation suggested by other authors.

Temperature (°C)	Growth Rate ($\mu\text{m/hr}$)
400	1.94 ± 0.07
500	2.42 ± 0.12
550	2.41 ± 0.11
600	2.42 ± 0.13

Table 7.5: Temperature dependence of GaAs growth rate, from the GaAs cap thicknesses determined by XRD.

As shown in Table 7.5, the GaAs cap growth rate is independent of temperature for $500\text{ °C} \leq T_g \leq 600\text{ °C}$. This is indicative of mass-transport-limited growth (Figure 2.4). Gérard *et al.* [77] suggested that the segregation process may be minimized by suitable kinetic adjustments during the cap layer growth. In the mass-transport-limited regime the growth may be less susceptible to a kinetic rearrangement of group III atoms, allowing a reduction in the In-Ga exchange reaction. At 400 °C, which is in the surface-kinetic-limited regime, the growth kinetics may play a larger role. A strong T_g -dependence in the surface reconstruction during growth was shown in Figure 7.15. This results from the incomplete decomposition of the TBAs molecules

at lower T_g which may contribute to the apparent segregation enhancement under these conditions.

Guille *et al.* [8] suggested that very high GaAs growth rates could beat the In-Ga exchange rate, although this was not the case for up to $0.5 \mu\text{m/hr}$. Recent results [93] for MBE-grown InGaAs/GaAs structures at $5.1 \mu\text{m/hr}$ and 500°C have noted a reduction in segregation due to the rapid surface coverage. At our higher temperatures the GaAs growth rate of $2.4 \mu\text{m/hr}$ may be sufficient to discourage segregation. At lower temperatures the reduced GaAs growth rate allows the segregation process to occur more prominently.

The time-resolved RDS study described in Section 7.6.1 did not indicate any pronounced segregation during GaAs overgrowth. In contrast, clear evidence of In segregation was observed during ALE growth (Section 7.4) which has a much higher cation surface mobility than conventional MOVPE. This mobility produces the smooth interfaces which are associated with the technique. Unfortunately, the lack of As overpressure leads to enhanced exchange reactions between incoming Ga atoms and the underlying In [9, 84]. While ALE produces interfaces that are highly uniform and smooth, they suffer from reduced abruptness. Section 7.4 showed that In segregation cannot be eliminated in the ALE growth for any usual growth temperature.

We conclude that the combination of growth in a mass-transport-limited regime, high growth rate, and low cation surface mobility aid in reducing segregation effects in the 1 ML structures produced at the higher temperatures. For lower- T_g samples, the XSW data are indicative of enhanced In segregation. This arises because of surface kinetics effects: lower As coverage on the growing surface, and the lower GaAs growth rate. Although these factors are a direct consequence of the reduced temperature, the temperature itself is not the important parameter *per se*.

ALE Results (Revisited)

It is worth reconsidering the XSW results for ALE-grown samples. The data were interpreted in terms of In atoms arranged in single $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers, with $x < 1$. This interpretation was used because the experimental values of P^H were found to

be less than the ideal value. However, this neglected the In segregation directly observed using RDS. Model (i) described in this section predicts that the segregated In atoms are arranged in alloy layers, with the layer composition graded along the growth direction. This model does predict values of $P^H < 1.15$, although the lowest value predicted by the model is $P^H = 1.137$, for $\sigma = 1.0$. This value is still greater than the highest P^H measured for the ALE samples. It is possible that the ALE samples contain less than one complete ML of incorporated In, as suggested previously, and that the In distribution also follows the scheme of model (i). In such a case, however, the total amount of incorporated In and the segregation coefficient would be highly correlated parameters and could not be separated.

If model (i) describes a segregated In-distribution, then how can the XSW results for the low- T_g MOVPE samples be explained? It is possible that at the lower temperatures the InAs grows in a 3-dimensional mode, and forms islands with greater than 1 ML height, even prior to GaAs overgrowth. The direct observation of such islands would be difficult since the island heights would still be quite small, but could perhaps be achieved using atomic-resolution scanning probe microscopy.

The XSW and PL results for the 1 ML MOVPE samples would also be consistent with the incorporation of more than 1 ML of InAs at the lower growth temperatures, and an InAs incorporation rate which decreases with increasing T_g . In homoepitaxy, Watkins *et al.* [138] observed the opposite behaviour, i.e. an increasing InAs growth rate with increasing T_g . For the SQW growth sequences the heteroepitaxial strain likely affects the In incorporation, so the homoepitaxy results do not preclude the possibility of excess In in the MOVPE samples. It is not possible to determine the In incorporation with sufficient precision to address this issue. The next section describes the results of X-Ray absorption measurements performed at SSRL.

7.7 XAFS Study

This section will begin by describing the reflectivity scans used for sample alignment. The experimental XAFS data will then be presented, followed by a discussion of the data analysis.

7.7.1 Reflectivity Measurements

The sample crystals were aligned in the GIXAS apparatus as discussed in Section 6.7. Reflectivity ($R = I_1/I_0$) measurements were made as a function of glancing angle, θ , while simultaneously measuring the In K_{α} -fluorescence with the 13-element detector. A representative dataset obtained at 200 eV above the In K-edge ($E_0=27940$ eV) is shown in Figure 7.28. The background In-fluorescence was subtracted from the experimental curve using a second curve obtained below the In K-edge.

The figure also shows the results of simulations for the reflectivity and the electric field intensity in the In layer based on the method of Sections 4.3.1 and 4.3.2. The simulations used the GaAs cap thickness measured by HRXRD (92 Å) for this sample. The theoretical curves were given a geometrical correction to account for the variation in the sample cross section illuminated by the beam. Figure 6.12 shows that for $\sin \theta < h/L$ the reflectivity is slightly reduced because the beam height, h , is larger than the effective sample height, although the entire sample surface is illuminated by the beam. For $\sin \theta > h/L$ the reflectivity is unaffected by geometric effects. However, the beam can not illuminate the whole sample surface, and so the In fluorescence is slightly reduced. The simulated curves in Figure 7.28 also include a Gaussian correlation function (FWHM=19 mdeg) to account for the beam divergence.

Following sample alignment and reflectivity measurements, the samples were positioned at angles greater than the critical angle for the polarization-dependent XAFS measurements. For the measurements presented here, incidence angles near $\theta=0.2^\circ$ were used. XAFS measurements were made by varying the photon energy according to Table 6.4 and recording the incident and reflected intensities, as well as the In K_{α} -fluorescence.

7.7.2 XAFS Analysis: Preliminaries

The processing of raw XAFS data involves deglitching to remove Bragg peaks, and the summation of all scan data in a given series. This was accomplished using APL (A Programming Language) routines developed by Andrew Seary. The EXAFS, χ , was then separated from the data using the AUTOBK program [139]. This involved

Figure 7.28: (a) Experimental reflectivity (circles) for the 1 ML InAs SQW grown at 500 °C measured at 28140 eV in the $E_{||}$ -polarization. (b) The In K_{α} -fluorescence yield (circles) measured for the same sample. Each curve also shows the results of simulations as described in the text.

pre-edge background removal using a linear fit; normalization to the edge jump to put the data on a per-atom basis; and postedge background removal. In the last step a smoothly-varying background function which approximates the absorption from an isolated absorbing atom, $\mu_0(E)$, was subtracted from $\mu(E)$ to give $\chi(E)$ (see Equation 4.4).

AUTOBK uses a fourth-order polynomial spline with knots equally spaced in k -space to minimize the low- R background in the Fourier transform (FT) of $k\chi(k)$. A good background subtraction will give a FT containing almost no low- R components aside from leakage from the first shell. For the In K-edge XAFS, the AUTOBK program was used to minimize the background below the first shell automatically by comparing the data with a reference (FEFF6b) spectrum. AUTOBK subtracts a trial spline function from the data and then transforms the data into R -space. The spline is then allowed to vary iteratively until the low- R region is optimized in comparison with the reference. In this background subtraction AUTOBK was allowed to adjust the edge energy, E_0 , to reduce the low- R contributions, rather than holding E_0 fixed at the inflection point (the point on the edge where $d^2\mu(E)/dE^2 = 0$). This approach will be discussed in Section 7.7.4.

Figure 7.29 shows the In K-edge XAFS from an InAs reference powder. These transmission data were obtained at beamline X23A2 using Si(311) MC crystals. Since the structure of the reference is well known, it provides a useful test of the analysis procedure. Superimposed on the data is the AUTOBK spline background. For the large k -space range of these data the spline contained 17 knots. For the InAs SQW samples 15 knots were used. The dataset shown in Figure 7.29 has been adjusted by removal of the pre-edge line and normalized by the edge jump. Following this procedure the detailed data analysis may proceed.

7.7.3 EXAFS Analysis: Curve Fitting

As discussed in Chapter 4, experimental EXAFS $\chi(k)$ data may be analyzed using either a reference spectrum or a theoretical model. The InAs SQW samples were

Figure 7.29: In K-edge XAFS from an InAs powder sample obtained in transmission at beamline X23A2 at the NSLS (heavy line) and the AUTOBK background (light line). The pre-edge linear background was removed from both curves and the curves were normalized by the edge jump.

analyzed using both methods for comparison. For the InAs reference powder the In-As bond lengths were fitted using a FEFF6b model to evaluate the precision of the fits obtained with this method.

The FEFF model was produced using the InAs lattice constant, $a_{\text{InAs}} = 6.0584 \text{ \AA}$, and the zincblende structure. In the model an In atom at the center of the crystal was defined as the absorber and the EXAFS was calculated. The first shell contains four As atoms located a distance of $2.623 \text{ \AA}$ from the absorbing atom. FEFF6b uses a curved-wave model to calculate the phase shifts, effective scattering amplitudes, and single and multiple scattering EXAFS and XANES spectra [44].

In this thesis all EXAFS curve-fitting was done in k -space, although fitting in

R -space is also possible. After background removal the data were transformed into R -space using a 10% Gaussian window function. The FT magnitude for the experimental InAs reference data appearing in Figure 7.30, shows that the EXAFS consists mainly of an In-As first shell peak. Second and higher shells are smaller by more than an order of magnitude. This suggests that the determination of bond-lengths and coordination numbers beyond the first shell is essentially impossible for such samples. Given that the data shown in Figure 7.30 were obtained for a concentrated powder specimen the second shell analysis for dilute samples (e.g. InAs MLs in GaAs) is even more impractical.

Figure 7.30: Fourier transform of the k -weighted In K-edge EXAFS from the InAs powder sample. A 10% Gaussian window was used in the transform over the range $k=0.52 \rightarrow 16.15 \text{ \AA}^{-1}$. The arrow indicates the maximum R -value used in the Fourier-filtering.

The next analysis step involved Fourier-filtering the data by selecting a range

in R -space to include only the first shell. In Figure 7.30 the data from 0.03 Å to 2.86 Å were included. This limited range of data was then back-transformed into k -space where the curve-fitting determines the first shell structure.

From Chapter 4, the EXAFS, $\chi(k)$, for K-edge absorption is expressed as

$$\chi(k) = \sum_i B_i(k) \sin[2kR_i + 2\delta(k) + \phi_i(k)] \quad , \quad (7.18)$$

where the sum is taken over all atoms, i , located at distances R_i from the absorbing atom, and the phase shifts, $\delta(k)$ and $\phi_i(k)$, arise from the interaction between the absorber and the backscatterer, respectively. The amplitude function, $B_i(k)$, was defined as

$$B_i(k) = \frac{N_i^*}{kR_i^2} S_0^2 F_i(k) e^{-2R_i/\lambda_i(k)} e^{-2k^2\sigma_i^2} \quad , \quad (7.19)$$

where

$$N_i^* = 3N_i \cos^2(\theta_i) \quad . \quad (7.20)$$

Here N_i is the number of atoms of type i located at an average distance R_i from the absorber and the other quantities were defined in Chapter 4.

Figure 7.31a) shows the Fourier-filtered first shell (FFFS) superimposed on the raw EXAFS data. The observation that the data consist mainly of first-shell EXAFS is clearly confirmed. Figure 7.31b) shows the FFFS data, as well as the fit using the FEFF model. The data were least-squares-fitted using the theoretical amplitude, $B_i(k)$, and phase, $(2\delta(k) + \phi_i(k))$ for the In-absorber and As-first-shell backscatterer. In the fits the variable parameters were S_0^2 , R , σ^2 and ΔE_0 , which allows for an offset between the theoretical and experimental values of E_0 , obtained from AUTOBK. The fits were carried out using only the data for $k > 4 \text{ Å}^{-1}$ to minimize the effect of the energy shift on the In-As bond length, which is most sensitive to such a discrepancy. The fitting was done using the WINXAS software package.¹

The results of the fitting are: $S_0^2 = 1.03 \pm 0.07$ and $\sigma^2 = 0.0047 \pm 0.005$, while the In-As bond length is $R = 2.625 \pm 0.004 \text{ Å}$. The error bars indicate the values which double the squared residuals in each parameter when the other values were allowed to float. Figure 7.31 clearly shows the agreement between the data and the FEFF

¹WINXAS 7.0 ©Thorsten Reesler.

Figure 7.31: a) Raw EXAFS data from the InAs powder specimen and the Fourier-filtered first-shell contribution, due to In-As bonds. b) Fourier-filtered first-shell data (solid circles) and the fit to the data obtained with the FEFF predictions.

model. In fact, the agreement between the fitting result and the known In-As bond length (2.623 Å) is outstanding. It must be noted that results of this accuracy were not obtained if the data were fitted to lower k -values.

Given this basis in EXAFS analysis we now consider the results for single ML samples, obtained in the glancing-incidence geometry.

7.7.4 EXAFS Analysis: SQW Samples

Figure 7.32 shows XANES spectra for the ML samples in the parallel and perpendicular polarizations, as well for the InAs powder. The XANES is related to the electronic structure and bonding geometry of the absorbing atom, so it is reassuring to see the agreement between the data for different samples, and between the two polarizations.

The background subtraction for the 1 ML samples again used AUTOBK, with a reference $\chi(k)$ obtained from a FEFF model for a single InAs layer in GaAs. The data were then Fourier-filtered to fit the first shell data. The magnitudes of the Fourier-transformed data are shown in Figure 7.33.

In the parallel geometry, the FTs are qualitatively similar between the samples grown at 500 and 600 °C, consisting primarily of a large first shell peak centred near 2.1 Å. The peak position is shifted downwards from the actual bond length because of the EXAFS phase shift (Equation 7.18). Small differences exist between the higher-order peak positions in the two samples. The first shell peaks in the $E_{\perp}$ geometry line up very well with one another. The 500 °C sample is different from the other two in its second shell, however, and seems to exhibit a splitting. It is not clear whether this is a real effect or statistical artifact. The low- R region exhibits a spurious feature related to the background. The nodes above and below the second shell line up very well in the three samples. In the InAs/GaAs SQW FEFF model, the central In absorbing atom is surrounded by an arrangement of backscatterers as listed in Tables 7.6 and 7.7. The model used the MET to evaluate the In-As planar distance and the atomic locations were calculated from the geometry of the zincblende lattice.

Tables 7.6 and 7.7 follow the notation of Zabinsky *et al.* [44] to enumerate the

Figure 7.32: In K-edge XANES from the 1 ML InAs films, obtained in both the parallel ($E_{\parallel}$) and perpendicular ($E_{\perp}$) geometries and growth temperatures as indicated. The top spectrum was obtained from the InAs reference powder in transmission. The spectra have been normalized and offset for clarity. The dotted vertical line denotes the edge energy.

Figure 7.33: Fourier transform magnitudes for k -weighted In K-edge EXAFS in $E_{||}$ (top curves) and $E_{\perp}$ polarizations (bottom curves) for 1 ML samples and growth temperatures as indicated. A 10% Gaussian window was used in each transform over a range of about $k=0.7 \rightarrow 12 \text{ \AA}^{-1}$.

Backscatterer	R (Å)	C_{cw}	N_{Γ}	n	Type
As	2.576		2	2	SS, first shell
As	2.576	100.00	2	2	SS, first shell
In	3.997	61.13	2	2	SS, second shell
In	3.997	0.69	2	2	SS, second shell
Ga	4.150	35.16	8	2	SS, third shell
	4.575		2,2,4,4	3	MS
	4.587		8,8	3	MS
	4.729		8	3	MS
As	4.755	36.10	4	2	SS, fourth shell
As	4.755	8.91	4	2	SS, fourth shell
As	4.879	0.07	2	2	SS, fifth shell
As	4.879	3.89	2	2	SS, fifth shell

Table 7.6: The most important paths in the InAs SQW FEFF calculation for the parallel geometry. Here R is the effective path length; C_{cw} is the importance in percent of each path relative to the first SS path; the degeneracy, N_{Γ} , is the number of equivalent paths; n indicates the number of legs for each path; and path types include “SS” single scattering and “MS” multiple scattering. Some of the MS contributions involve several different paths (with degeneracies shown) and these are not listed completely. The C_{cw} contribution of the first pair of As atoms in the first shell is negligible, but FEFF erroneously assigns a value of 100.00.

paths out to 5 Å. Note that the degeneracy of some of the paths is lifted when the $E_{\parallel}$ orientation is used. The FEFF calculation includes the polarization by aligning the electric vector along the (110) or (001) crystal axes, for the $E_{\parallel}$ and $E_{\perp}$ cases, respectively. In the experiment the $E_{\parallel}$ -orientation was not exactly along the (110)-axis because the sample was rotated slightly to manipulate the unwanted Bragg peaks. A simple geometric calculation verifies that the rotation does not affect the results, and that only two of the first shell As atoms contribute to the EXAFS. Multiple scattering refers to any path more complicated than a simple absorber-backscatterer interaction. In the following the discussion will be limited to the first shell, containing In-As bonds.

Figures 7.34 and 7.35 show the raw EXAFS data and the results of fitting the FFES using the FEFF phases and amplitudes. The fits were carried out with the variable parameters S_0^2 , R , σ^2 and ΔE_0 . Results of the fitting for the 1 ML samples

Backscatterer	R (Å)	C_{cw}	N_{Γ}	n	Type
As	2.576	100.00	4	2	SS, first shell
In	3.997	1.05	4	2	SS, second shell
Ga	4.150	62.85	8	2	SS, third shell
	4.575		4,8	3	MS
	4.587	13.48	16	3	MS
	4.729	5.85	8	3	MS
As	4.755	8.93	8	2	SS, fourth shell
As	4.879	29.88	4	2	SS, fifth shell

Table 7.7: The most important paths in the InAs SQW FEFF calculation for the perpendicular geometry. Here R is the effective path length; C_{cw} is the importance in percent of each path relative to the first SS path; the degeneracy, N_{Γ} , is the number of equivalent paths; n indicates the number of legs for each path; and path types include SS and MS. The first MS contribution involves two different paths (with degeneracies shown).

are tabulated in Table 7.8. In all cases the experimental In-As bond lengths agree with the expected value ($R=2.576$ Å) within the uncertainties in the fitting. Similar (In L_3 -edge) results were obtained by Woicik *et al.* [2], although the k -space range was limited to $4 \rightarrow 7.2$ Å⁻¹ by the intervening L_2 -edge. The K-edge measurements presented here have the advantage of an extended k -space range which gives higher precision.

It is well known that ΔE_0 and R can be highly correlated parameters [140]. In the background subtraction, AUTOBK was allowed to adjust E_0 to minimize the low- R

Mode	Sample	S_0^2	R (Å)	σ^2 (Å ²)	N^e	R^e (Å)	N^e/N^{th}
$E_{ }$	500 °C	1.32 ± 0.16	2.571 ± 0.007	0.0050 ± 0.0008	4.6 ± 0.4	2.568 ± 0.006	1.3 ± 0.1
	600 °C	1.01 ± 0.06	2.575 ± 0.004	0.0028 ± 0.0004	4.7 ± 0.6	2.573 ± 0.008	1.3 ± 0.2
$E_{\perp}$	400 °C	0.85 ± 0.08	2.574 ± 0.006	0.0035 ± 0.0006	4.6 ± 0.5	2.571 ± 0.007	0.97 ± 0.10
	500 °C	0.98 ± 0.13	2.585 ± 0.008	0.0050 ± 0.0010	4.4 ± 0.6	2.581 ± 0.008	0.92 ± 0.12
	600 °C	0.83 ± 0.09	2.571 ± 0.006	0.0032 ± 0.0007	4.7 ± 0.6	2.567 ± 0.009	0.99 ± 0.13

Table 7.8: Fit parameters obtained from the experimental In-As first shell EXAFS. The data were fitted using both FEFF and the empirical InAs standard as described in the text. The error bars indicate the values which double the squared residuals in each parameter when the other values were allowed to float.

background of the fluorescence EXAFS with respect to the FEFF standard. This led to a choice of E_0 slightly different than the inflection point (up to a difference of nearly 8 eV in the SQW samples). This occurs, in part, because of the inaccuracy of FEFF in estimating the correct position of $k=0$. In the EXAFS curve-fitting, the variable parameter ΔE_0 compensates for this discrepancy. To investigate the effect of this energy shift on the bond-lengths the analysis procedure was repeated holding E_0 fixed at the inflection point in the AUTOBK background removal. When the resulting SQW EXAFS datasets were then fitted using the FEFF models, it was found that the ΔE_0 shifts were reasonably similar for all samples (between 1.8 and 4.5 eV) and the best-fit In-As bond lengths were within the error bars quoted in Table 7.8.

Likewise, the data were fitted in a comparative manner by using an “internal reference”. Using the best-fit ΔE_0 for one of the samples, the datasets for the remaining samples were curve-fitted with this fixed ΔE_0 . This procedure was repeated several times, by rotating through in the selection of the internal reference. Again the bond lengths agreed with the results shown in Table 7.8 within the quoted error bars. These alternative approaches helped confirm the validity of the analysis approach leading to the results in Table 7.8.

In addition to the FEFF fits, the present data were fitted using the InAs reference $\chi(k)$ as an empirical phase, $\phi(k)$, and amplitude, $|f(k)|$, standard,

$$\chi(k) = \frac{N^c}{k(R^c)^2} |f(k)| \sin[2kR^c + \phi(k)] \quad . \quad (7.21)$$

In this case the variable parameters in the fits were the coordination number, N^c , the In-As bond length, R^c , and an offset ΔE_0 . Note that in this case N^c contains contributions from the coordination number, as well as the from the EXAFS Debye-Waller factor, $e^{-2k^2\sigma^2}$. The results are given in Table 7.8 from which it is seen that the bond lengths obtained using the empirical method agree very well with those obtained using the theoretical calculation. There does not appear to be any connection between the In-As bond lengths and the growth temperature.

The parameter N^{th} in Table 7.8 refers to the theoretical number of nearest-neighbours based on the geometry ($N^{th} = N_i^*$). According to Equation 7.20 this

is calculated from the angle, θ , between the incident electric vector and the direction of the bond. Using the MET to predict the In-As plane spacing, the geometry gives $N^{th}=3.61$ in the parallel geometry and $N^{th}=4.78$ in the perpendicular geometry. These values take into account the 2 and 4 atoms which contribute in the $E_{\parallel}$ and $E_{\perp}$ -orientations, respectively.

Although the bond length fitting results agree quite well with the expected values, the effective coordination numbers show larger discrepancies. It is generally more difficult to obtain precise N -values because they depend on the EXAFS amplitude and so normalization errors directly affect the results. Also, there is an outstanding question of the transferability of the amplitude and phase data obtained in transmission, when one attempts to use this to model glancing-incidence data. For the $E_{\parallel}$ -orientation the fitting results are larger than expected, and for the $E_{\perp}$ -orientation the results are slightly lower than expected.

In the FEFF fitting the parameters S_0^2 and $\exp(-2k^2\sigma^2)$ can also be correlated [140]. Each of these parameters affects the EXAFS amplitude making it slightly difficult to separate the two contributions, although the exponential term does have a k -dependence. These parameters may be studied in more detail using temperature-dependent measurements, for example.

If each InAs SQW sample contained In atoms arranged in a single layer, then the XSW results (Section 7.6.4) might be interpreted in terms of reduced bond length compression at lower values of T_g . Assuming coherency with the GaAs substrate, the experimental values of P^H would then correspond to In-As bond lengths of $R=2.612$ Å (400 °C), $R=2.594$ Å (500 °C) and $R=2.576$ Å (550, 600 °C). Clearly the EXAFS bond lengths do not support this single-layer interpretation for the lower values of T_g .

The next section presents the PL data which are used to evaluate the optical properties of the SQW samples and for comparison with the structural (XSW) studies.

Figure 7.34: k -weighted In K-edge EXAFS, $k\chi(k)$, with $E_{||}$ -polarization, from 1 ML InAs films and growth temperatures as indicated. The top spectrum was obtained using an InAs reference powder in transmission. Superimposed on the data are the fits to the Fourier filtered first-shell contributions, which correspond to the In-As near neighbour bond lengths.

Figure 7.35: k -weighted In K-edge EXAFS, $k\chi(k)$, with $E_{\perp}$ -polarization, from 1 ML InAs films and growth temperatures as indicated. Superimposed on the data are the fits to the Fourier filtered first-shell contributions, which correspond to the In-As near neighbour bond lengths.

7.8 PL Results

The PL spectra for the 1 ML samples are shown in Figure 7.36. For the sample grown at 400°C the spectrum shows very weak In-excitonic luminescence. The feature labeled ‘DAP’ represents donor-acceptor pair (1.490 eV) and free-to-bound (1.493 eV) transitions at carbon impurities, resulting from incomplete TBAs decomposition which leads to carbon incorporation in the crystal. For the remaining samples, the PL emission energies increase with growth temperature, while the linewidths generally decrease. An exception is the sample with $T_g = 530^\circ\text{C}$, exhibiting particularly sharp luminescence.

For the 1/2 ML samples (Figure 7.37), 400°C is again seen to be unsuitable for good optical material, despite the more promising XSW results. The spectrum is dominated by the carbon impurity features. The brightest 1/2 ML In-luminescence is observed for the sample with $T_g = 600^\circ\text{C}$.

Figure 7.38 shows a comparison between the structural and optical properties. The data suggest a correspondence between the decreasing P^H and the increasing PL peak energies as a function of growth temperature in the 1 ML samples. As well, the PL linewidths decrease dramatically with increasing T_g . This is mirrored somewhat by the increasing coherent fraction. These characteristics may be attributed to a trend towards more perfect, δ -like InAs layers, being particularly evident in the 530-550°C range.

Previous treatments [84] of the effect of In segregation on optical emission found that with decreasing T_g the transitions are shifted towards lower energies and then saturate at minima which, the authors argued, correspond to minima of segregation. In that case, however, the transition energy vs. T_g curves were concave up. From Figure 7.38, our results do not reproduce these observations. Rather, the PL energies increase with increasing T_g , and may approach limiting behaviour at temperatures beyond those considered here. We point out that the curve is concave down in this case. Thus, these results do not necessarily indicate temperature-dependent segregation.

Previously in this work we showed that the large coherent positions observed by XSW in the low- T_g samples were consistent with model (ii) which supposed In

Figure 7.36: PL spectra for a series of 1 ML InAs samples, with growth temperatures as indicated. The spectra were normalized to a peak height of unity and offset for clarity. The quantities in parentheses denote the absolute peak amplitudes prior to normalization.

Figure 7.37: PL spectra for a series of $1/2$ ML InAs samples, with growth temperatures as indicated. The spectra were normalized to a peak height of unity and offset for clarity. For the 500 °C and 600 °C samples the peak energies indicated refer to the more intense, higher energy peaks.

Figure 7.38: Summary of the XSW and PL results for the main group of MOVPE samples. The circles and squares correspond to 1 ML and 1/2 ML samples, respectively. For the PL data, the uncertainties are given approximately by the symbol size. The solid lines are guides for the eye.

incorporation in islands rather than in graded $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers. If these islands have lateral extents greater than the exciton radius, then the net effect would be a decrease in the emission energy due to the fact that the exciton samples a potential well of thickness significantly greater than 1 ML, while maintaining an average layer thickness of approximately 1 ML [5, 6].

The lack of any clear trend for the 1/2 ML samples is noteworthy; since the MOVPE InAs growth exposures for these samples were half the corresponding full ML exposures, we might expect similarities between the two series. The lack thereof may be related to details of the growth mechanism at the subML scale. For example, the growth could take place in either 2-dimensional or 3-dimensional modes, or could involve compositional alloying, the details of which are difficult to resolve.

The final section of this chapter involves a study of both In-As and Ga-As bond-lengths occurring in ternary alloy films grown in InP. This study will demonstrate the effects of both tensile and compressive strains in pseudomorphic epitaxy.

7.9 Bond-length Distortions in $\text{InGaAs}/\text{InP}(001)$ Heterostructures

As mentioned in Section 5.1, ternary alloys of $\text{In}_x\text{Ga}_{1-x}\text{As}$ were grown by MOVPE in order to study the effect of strain on the bond-length distortions. This work was done in collaboration with Dr. Woicik at NIST. When $x=0.53$, the ternary lattice constant obtained from Vegard's law (Equation 5.3) is equal to the value for InP ($a_{\text{InP}}=5.869 \text{ \AA}$). For an epitaxial film of this composition buried in InP(001), there is no net strain and so the In-As and Ga-As bond lengths should have the same values as for a bulk alloy with this composition, i.e. in agreement with the results of Mikkelsen and Boyce [54]. By varying the composition it was possible to study this lattice-matched (LM) case, as well as the cases of tensile ($x < 0.53$) and compressive ($x > 0.53$) strain. In the limiting cases the strains are $\varepsilon_{\parallel}=+3.8\%$ for $x=0$ and $\varepsilon_{\perp}=-3.1\%$ for $x=1$.

The samples were grown in a horizontal quartz reactor at 100 Torr and 560 °C.

SUMITOMO InP(001) Fe-doped substrates were used with no additional cleaning. Each growth was preceded by the growth of an InP buffer layer (~ 800 Å) using TMin at $14.8 \mu\text{mol}/\text{min}$ and TBP at $409 \mu\text{mol}/\text{min}$. The TMin flow was then reduced to the desired flow rate for the rest of the structure, and an additional, thin InP buffer layer was grown at the new flow rate. In order to form abrupt interfaces with minimal group V mixing, the growth interruption scheme of Holmes *et al.* was employed [141]. Following the InP buffer growth, the growth was interrupted first under TBP for 0.5 sec, and then under H_2 for 0.5 sec. The $\text{In}_x\text{Ga}_{1-x}\text{As}$ layer was then deposited by simultaneously flowing TEGa, TMin and TBAs. Following the alloy growth another pair of interruptions of 0.5 sec under H_2 , and 0.5 sec under TBP was used. A thin InP cap layer was then deposited at the same TMin flow rate as for the alloy layer. Holmes *et al.* found that the elimination of TBAs from the growth interruptions leads to a reduction in interface effects for the InGaAs/InP interface. The alkyl flow rates are given in Table 7.9. For all three samples a TBAs flow rate of $57.2 \mu\text{mol}/\text{min}$ was used to give a V/III ratio of 4.8.

Sample	TMin ($\mu\text{mol}/\text{min}$)	TEGa ($\mu\text{mol}/\text{min}$)	x^v	x	t (Å)	t_{cap} (Å)
Tensile	4.02	7.80	0.34	0.21	65	83
LM	7.91	3.97	0.67	0.50	1095	85
Compressive	9.30	2.59	0.78	0.74	53	93

Table 7.9: Alkyl flow rates and input vapour phase composition, x^v , for MOVPE growth of InGaAs layers on InP. The solid phase composition, x , thickness, t , and cap thickness, t_{cap} were determined by XRD.

The strained layer thicknesses and compositions were determined by HRXRD as shown in Figure 7.39. To ensure coherency of the layers with the substrates, the strained layers were necessarily very thin. It was verified using AFM that layers of these thicknesses and composition were below the critical thicknesses for pseudomorphic growth.

In the HRXRD measurements, the slit shown in Figure 6.5 was replaced by a circular pinhole of approximately 2 mm diameter to collimate the beam and allow position-dependent measurements across each sample. The results for the LM sample

are given in Table 7.9. From the HRXRD data obtained at several positions (Figure 7.40) it was found that the composition is not laterally uniform. This is a problem intrinsic to this horizontal reactor which may be related to gas-phase depletion effects downstream. Insufficient data were obtained to quantify this spread in the strained samples and so the XRD results should not be considered mean values of x , t or t_{cap} . A comparison between the In fraction in the input vapour and the measured values is shown in Figure 7.41. The ratio x/x^v is called the distribution coefficient [21].

The XAFS measurements were performed at beamline X23A2 by monitoring the Ga and As fluorescence yield as a function of incident photon energy and flux above both the Ga ($E_0 = 10367$ eV) and As ($E_0 = 11867$ eV) K-edges. The data presented here were obtained using either a Lytle detector or a single-element Si detector. A glancing-incidence geometry was used, although the alignment was much less rigorous than for the InAs SQW measurements, partly because of the lower edge energies involved. The critical angles are 0.23° and 0.20° at 200 eV above the Ga and As edges, respectively. Each 1/4 wafer sample was adhered to an Al plate of thickness ~ 2 mm using a melted wax layer, and then the plate was taped to a small RADIO SHACK computer fan. In order to avoid contamination to the spectra arising from Bragg peaks the samples were spun around their surface normals during data acquisition using the fan. The incidence angles were adjusted using a stack of washers mounted under the downstream end of the fan.

For this study the data were analyzed using empirical phase and amplitude standards obtained from powder samples in transmission. Powder data from GaAs, InAs and GaP standards were processed with AUTOBK using the methods described in Section 7.7. As a reliability check the powder datasets were analyzed using FEFF6b models for the GaAs and GaP crystals at the Ga K-edge, and GaAs and InAs crystals at the As K-edge. The raw transmission data and the fits to the FFFS contributions are shown in Figures 7.42 and 7.43.

These figures clearly show that, with the exception of the InAs powder measured at the As K-edge, the EXAFS data contain significant contributions from the first shells, as well as second and higher-order shells. This is also seen in the FTs shown in Figure 7.44. In particular the GaP powder has a second shell of comparable amplitude

Figure 7.39: X-Ray rocking curve data obtained near the InP(004) symmetric substrate reflection, for $\Delta\theta = \theta - \theta_B$. The data for the strained $\text{In}_x\text{Ga}_{1-x}\text{As}$ films are indicated by circles and the solid lines indicate the results of dynamical simulations using the x -values indicated and the layer thicknesses as described in the text.

Figure 7.40: X-Ray rocking curve data obtained near the InP(004) symmetric substrate reflection. The data were obtained using pinhole-collimation at different positions on the nominally lattice-matched sample (the horizontal and vertical positions are given in mm). The data are indicated by circles and the solid lines indicate the results of dynamical simulations using the x -values indicated and the layer thicknesses as described in the text.

Figure 7.41: Indium composition, x^v , in the input vapour phase compared with the composition determined by XRD (circles) and EXAFS (squares and error bars) measurements. The solid line corresponds to a distribution coefficient of unity.

to the first shell. It is interesting to note the close correspondence between the Ga and As K-edge FTs for the GaAs powder over the whole R -range shown in the figure. After Fourier-filtering the data were fitted with the FEFF phases and amplitudes, yielding the results shown in Table 7.10. In the fits the variable parameters were S_0^2 , R , σ^2 and ΔE_0 . The agreement with the known bond lengths is excellent, except for the Ga-P bond length, in which case the expected value is just outside the error bar. Note that the As K-edge data indicate that S_0^2 depends upon the chemical environment of the absorbing atom in agreement with the observations of Li *et al.* [140].

Figures 7.45 and 7.46 show the *raw* k^2 -weighted Ga and As K-edge EXAFS data from the alloy layers, respectively. Comparing the data with the transmission data of Figures 7.42 and 7.43 it is clear that the alloy data consist mainly of first-shell

Figure 7.42: k^2 -weighted Ga K-edge EXAFS, $k^2\chi(k)$, for the GaAs and GaP powder specimens. Superimposed on the data are the fits to the Fourier-filtered first shell contributions, corresponding to the Ga-As and Ga-P nearest-neighbour bonds.

Figure 7.43: k^2 -weighted As K-edge EXAFS, $k^2\chi(k)$, for the GaAs and InAs powder specimens. Superimposed on the data are the fits to the Fourier-filtered first shell contributions, corresponding to the As-Ga and As-In nearest-neighbour bonds.

Figure 7.44: The magnitudes of the Fourier transforms of the k^2 -weighted Ga and As K-edge EXAFS, $k^2\chi(k)$, from the reference powders. A 10% Gaussian window was used in each transform. The transform ranges (from top to bottom in the figure) were: $k=3.0 \rightarrow 14.6$ $\text{\AA}^{-1}$, $k=1.7 \rightarrow 17.7$ $\text{\AA}^{-1}$, $k=2.8 \rightarrow 17.7$ $\text{\AA}^{-1}$ and $k=1.9 \rightarrow 17.8$ $\text{\AA}^{-1}$.

		S_0^2	R (Å)	σ^2	R_0 (Å)
Ga K-edge	Ga-As	1.03 ± 0.07	2.449 ± 0.004	0.0048 ± 0.0004	2.448
	Ga-P	1.07 ± 0.05	2.365 ± 0.004	0.0051 ± 0.0005	2.360
As K-edge	As-Ga	1.03 ± 0.03	2.450 ± 0.002	0.0047 ± 0.0002	2.448
	As-In	0.80 ± 0.08	2.626 ± 0.005	0.0041 ± 0.0005	2.623

Table 7.10: Experimental determination of the bond lengths in powder standards from fitting with FEFF6b models. The known bond lengths, R_0 , are shown for comparison. The error bars indicate the values which double the squared residuals in each parameter when the other values were allowed to float.

contributions. Superimposed on the alloy EXAFS data are the fits to the FFFS contributions. At the Ga-edge, the first shell consists almost exclusively of Ga-As bonds. The strained samples, because they are thinner, also contain small contributions from Ga-P bonds at the interfaces. At the As-edge, however, the first shell contains both As-Ga and As-In bonds. The data were fitted using the appropriate phase, $\phi_i(k)$, and amplitude, $|f_i(k)|$, functions from the standards to a function of the form $\chi(k) = \sum_{i=1}^2 \chi_i(k)$, where the sum is taken over the first shell. In the fits only the coordination numbers, N_i , and the bond lengths, R_i , were varied. Table 7.11 shows the results of the fitting. The alloy compositions, x , determined from the coordination results are shown in Figure 7.41.

x	Ga K-edge	N	R (Å)	As K-edge	N	R (Å)
0.21	Ga-As	3.7 ± 0.3	2.477 ± 0.004	As-Ga	2.9 ± 0.5	2.475 ± 0.010
	Ga-P	0.2 ± 0.3	2.357 ± 0.25	As-In	1.4 ± 0.6	2.618 ± 0.021
0.50	Ga-As	4.1 ± 0.4	2.466 ± 0.005	As-Ga	1.9 ± 0.2	2.469 ± 0.005
	Ga-P			As-In	2.4 ± 0.2	2.611 ± 0.005
0.74	Ga-As	3.7 ± 0.2	2.463 ± 0.003	As-Ga	1.0 ± 0.2	2.465 ± 0.010
	Ga-P	0.2 ± 0.3	2.36 ± 0.09	As-In	3.4 ± 0.3	2.607 ± 0.003

Table 7.11: Experimental determination of the bond lengths and coordination numbers in $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys on $\text{InP}(001)$. Independent results obtained at both the Ga and As K-edges are tabulated. The error bars indicate the values which double the squared residuals in each parameter when the other values were allowed to float.

The FTs of the EXAFS data for the ternary alloys are shown in Figure 7.47. Comparing this figure with the FTs of the reference powders it is clear that the

Figure 7.45: k^2 -weighted Ga K-edge EXAFS, $k^2\chi(k)$, from pseudomorphic $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys on $\text{InP}(001)$. Superimposed on the raw data are the fits to the Fourier-filtered first shell contributions consisting mainly of Ga-As bonds.

Figure 7.46: k^2 -weighted As K-edge EXAFS, $k^2 \chi(k)$, from pseudomorphic $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys on $\text{InP}(001)$. Superimposed on the raw data are the fits to the Fourier-filtered first shell contributions which contain both As-Ga and As-In bonds.

second and higher shells are less well-defined. For the As K-edge data the first shell is less-well-defined than for the Ga edge. This is due to the fact that As absorbers are bonded to both Ga and In atoms, while Ga absorbers are bonded primarily to As atoms, with a small contribution due to Ga-P bonds.

To compare these results with theory, a random cluster calculation was performed following the formalism of Reference [62], which was briefly described in Section 5.1.3. In the present case the calculation was performed by relaxing the atoms within sixteen-bond $\text{In}_j\text{Ga}_{1-j}\text{As}$ clusters ($j=0,1,2,3$) embedded in virtual-crystal media. Figure 7.48 shows the resulting In-As and Ga-As bond lengths calculated for cubic clusters and for clusters that have been tetragonally distorted for pseudomorphic growth on InP(001). The bulk bond lengths follow the measurements of Mikkelsen and Boyce [54] and clearly do not support the VCA. The tetragonally-distorted bond lengths closely follow the experimental data. As mentioned at the beginning of this section, the bulk and strained bond lengths are predicted to be equal for LM films.

The downward slope of the strained-layer predictions clearly shows that the external strain imposed on the layer by the substrate opposes the natural bond-length distortions due to alloying. The tetragonally distorted In-As and Ga-As bond lengths are monotonically decreasing functions of composition, with a slight bowing due to the different C_{12}/C_{11} values for InAs and GaAs, which gives a nonlinear dependence to $a_{\perp}$. As in the case of bulk bond lengths, the strained bond lengths follow nearly parallel curves despite their different lengths and force constants. This experiment demonstrates that the bond lengths in strained-layer semiconductors deviate significantly from their bulk-alloy values, and the deviations are found to be uniform functions of the epitaxially-induced strain.

This concludes the presentation and the analysis of the experimental results obtained in this work. The next chapter will briefly summarize the results and suggest future directions.

Figure 7.47: The magnitudes of the Fourier transforms of the k^2 -weighted Ga and As K-edge EXAFS, $k^2\chi(k)$, for the ternary alloys. A 10% Gaussian window was used in each transform. For the As-edge the transforms were taken over a range $k=2.3 \rightarrow 14.5 \text{ \AA}^{-1}$. For the Ga-edge the transforms were taken over a range $k=2.3 \rightarrow 16.2 \text{ \AA}^{-1}$, except for the sample with $x=0.21$, where the transform window began at $k=2.5 \text{ \AA}^{-1}$.

Figure 7.48: Comparison between the experimentally-determined In-As and Ga-As bond lengths in pseudomorphic $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys on $\text{InP}(001)$ and the results of the random cluster calculation. The dotted lines are the calculated cubic (bulk) bond lengths and the solid lines are the calculated tetragonal (strained) bond lengths. The dash-dot line is the bulk virtual crystal approximation prediction. Note that the bulk and strained bond lengths coincide for $x=0.53$, i.e. the lattice-matched, zero-strain condition.

Chapter 8

Conclusions

This thesis has described the growth and characterization of ultrathin InAs SQWs in GaAs(001). Films 1 ML and 1/2 ML thick were grown by MOVPE and ALE and studied using a range of techniques, in which synchrotron measurements figured prominently.

XSW measurements of 1 and 1/2 ML InAs MBE films revealed that the layers do not contain complete In planes residing in well-defined positions. The XSW coherent positions were lower than expected for an ideally-strained ML and related to the composition, x , of single $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers, with In compositions less than unity because of inadequate growth rates or interface roughness. Measurements in samples grown at various temperatures clarified the competing requirements for the growth of abrupt interfaces. Buffer layer growth temperatures should be sufficiently high to promote smooth surfaces. InAs layers and the first several GaAs cap layers should then be grown at lower temperatures to reduce In segregation.

Similar coherent positions were measured in ALE-grown films [142]. 1 and 1/2 ML films grown using an ALE sequence which produces good optical emission were found to consist of $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers, with $x=0.79\pm0.07$ and $x=0.45\pm0.15$, respectively. In the subML case, this result suggests that the layer does not contain ML-high islands, but a uniform distribution of In atoms. In a sample grown with carefully controlled conditions to produce 1 ML/cycle GaAs cap layers, the In incorporation was slightly higher, at $x=0.89\pm0.14$. A study of the RDS transients during the growth of GaAs cap

layers showed that In segregation occurs to a large extent in ALE growth, regardless of the growth temperature or TMGa pulse duration. Models for the XSW parameters in the case of In segregation were unable to explain the low coherent positions measured in these films.

Growth of InAs SQWs in GaAs by conventional MOVPE was studied *in-situ* using multitransient RDS spectroscopy [143]. This method allowed the observation of the surface evolution from a GaAs $d(4\times4)$ -like spectrum under TBAs to the InAs (2×4) -like surface after 1 ML of InAs growth. Cap layer growth at various temperatures resulted in surface reconstructions characteristic of GaAs growth at those temperatures. No clear evidence of In segregation was observed with this technique.

These SQW structures were studied by HRXRD and synchrotron XSW [144] which showed that a growth temperature of 550 °C produced an InAs layer exhibiting the best structural properties: a coherent position of $P^H=1.15\pm0.02$ and coherent fraction $F^H=0.72\pm0.08$. This excellent layer quality was achieved as a result of growth in a mass-transport-limited regime, high GaAs cap growth rate and low cation surface migration rates. At lower temperatures the higher coherent positions were interpreted using a segregation model involving a terrace incorporation of In atoms. Here the enhanced segregation arises because of surface kinetics: lower effective As-overpressure and lower growth rate.

PL spectroscopy revealed an increase in the observed emission energies with increasing growth temperatures, accompanied by a decrease in linewidth. The sharpest luminescence was observed in a sample grown at 530 °C, suggesting that a range 530-550 °C is optimal for producing the best 1 ML films. At lower growth temperatures the lower emission energies arise because the islanded In distribution presents the excitons with a potential region greater than 1 ML thick.

In K-edge XAFS measurements were used to determine the In-As bond lengths using the polarization-dependent, glancing-incidence geometry. Bond lengths determined in MOVPE samples agree with the principle of strain accommodation through bond-bending, rather than bond stretching. No clear temperature-dependence was observed in these data, although they clearly showed that the samples grown at lower temperatures can not consist of single layers of In atoms, lending some credence to

the model deduced from the XSW data. The second-shell contributions were unfortunately too small to contribute to the structural analysis. A verification of the analysis technique was achieved by fitting EXAFS data from an InAs standard, obtained in transmission. Curve-fitting based on a FEFF6b model was used to determine the In-As bond length to within 0.002 Å of the accepted value.

To further elucidate the mechanisms of strain accommodation in heteroepitaxy the In-As and Ga-As bond lengths in a series of $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys of varying composition were determined using Ga and As K-edge EXAFS [68]. Fitting results using empirical amplitude and phase data agreed very well with a random cluster calculation. It was shown that the external strain imposed on the layer by the InP substrate opposes the natural bond-length distortions due to alloying.

A few directions for future research can be suggested at this time. Although the GaAs(004) substrate reflection was used for all XSW measurements presented here, other reflections can also be useful. To further clarify the In distribution in samples of this type it may be helpful to make XSW measurements using (111) or (224) reflections, for example. This is best accomplished by rocking the crystals through the Bragg angle at fixed photon energy and measuring the XSW in the usual way.

Other directions may involve completely different materials combinations. For instance, one could produce MOVPE SQW (or antiwell) structures containing several permutations and combinations of atoms from columns III and V of the periodic table: AlAs in GaAs; GaAs in InAs; AlAs in InAs; or InAs in AlAs. It might be particularly interesting to study mixing on the group V-sublattice: GaSb in GaAs; InAs in InP, and so on. The results should follow the principles elucidated in this thesis, although the experiments are not at all trivial. In particular, one must carefully consider the emission energies of the constituent elements to ensure that the XSW signal from the desired species can be distinguished from the signal arising from other elements. The sample preparation also requires careful planning. For instance, AlAs and GaAs are so closely lattice-matched that a single AlAs layer embedded in GaAs can not produce Pendellösung fringes in an HRXRD measurement. In this case one must apply creative methods to determine the amount of deposited Al. A very recent experiment by Lessmann, Brennan *et al.* used XSW to investigate $(\text{AlAs})_m(\text{GaAs})_n$

short-period SL structures through measurements at the 0th order SL satellite, as well as the substrate (004)-reflection [145].

Interesting EXAFS experiments can also be performed on technologically-relevant MOVPE-grown structures. For instance, issues of interface mixing in SL structures could be explored by performing EXAFS measurements at the various edges of the constituents. The DAFS technique is particularly promising for these applications. Measurements of fluorescence emission during glancing-incidence reflectivity scans (see Figure 7.28) can be used as a non-destructive tool for determining layer thicknesses and incorporated doses. This technique is particularly powerful in that it does not require crystalline material.

Finally, to build upon the sample preparation techniques yielding the favourable material quality and optical characteristics described in this thesis, it would be interesting to fabricate a CW laser diode employing an InAs SQW active region. As mentioned, injection lasers of this type have yet to be demonstrated. MQW structures could be produced with different GaAs barrier thicknesses or different periodicity to tune the emission wavelength for desired applications.

Appendix A

Calculation of X-Ray Structure Factors

In this section the details of the structure factor calculations will be presented. This will include the definitions of the conventional unit cell for the zincblende lattice in real and reciprocal space, and the details of the atomic form factors. The latter makes use of the atomic scattering factors and the anomalous contributions f' and f'' .

A.1 Zincblende Structure

The III-V semiconductors studied in this work share a common structure: the zincblende (cubic zinc sulfide) structure, consisting of two interpenetrating FCC lattices with cation and anions occupying the lattice positions in each of these sublattices. Figure A.1 shows the atoms in a conventional unit cell. The atomic coordinates are $(0,0,0)$; $(0, \frac{1}{2}, \frac{1}{2})$; $(\frac{1}{2}, 0, \frac{1}{2})$; and $(\frac{1}{2}, \frac{1}{2}, 0)$ for one species, while atoms of the second species occupy the positions $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$; $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$; $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$. These positions are defined relative to the lattice: $\vec{a}_1 = (a, 0, 0)$, $\vec{a}_2 = (0, a, 0)$ and $\vec{a}_3 = (0, 0, a)$ in real space, where a is the lattice constant. In reciprocal space the unit cell is defined by the vectors $\vec{b}_1 = \vec{a}_1/a^2$ and so on.¹

¹ Factors of 2π are not included, to be consistent with Batterman and Cole's notation which was used in Chapter 3.

Figure A.1: The crystal structure of zincblende compound semiconductors.

The structure factor is written as a Fourier sum over the atoms in the unit cell:

$$F_H = \sum_n f_n \exp(i2\pi \vec{H} \cdot \vec{r}_n) \quad . \quad (\text{A.1})$$

where the reciprocal lattice vector for the Bragg reflection having Miller indices (HKL) is

$$\vec{H} = H\vec{b}_1 + K\vec{b}_2 + L\vec{b}_3 \quad . \quad (\text{A.2})$$

Here $\vec{r}_n$ refers to the positions of atom n within the real space unit cell, i.e.,

$$\vec{r}_n = x_n\vec{a}_1 + y_n\vec{a}_2 + z_n\vec{a}_3 \quad . \quad (\text{A.3})$$

The prefactor f_n in Equation A.1 is the atomic form factor of atom n . When the effects of absorption are included, this is a complex quantity and may be written

$$f_n \equiv f_n^0 + f_n' + if_n'' \quad . \quad (\text{A.4})$$

The first real component, f_n^0 , describes the coherent scattering of X-Rays of wavelength λ incident upon the sample at Bragg angle θ . An analytic expression [146] may be used to describe the scattering from a given atom over a range of wavelengths and angles:

$$f_n^0\left(\frac{\sin\theta}{\lambda}\right) = \sum_{i=1}^4 a_i \exp\left[-b_i \left(\frac{\sin\theta}{\lambda}\right)^2\right] + c \quad . \quad (\text{A.5})$$

The coefficients in the expansion for elements of interest are listed in Table A.1.

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
Ga	15.2354	3.06690	6.70060	0.241200	4.35910	10.7805	2.96230	61.4135	1.71890
As	16.6723	2.63450	6.07010	0.264700	3.43130	12.9479	4.27790	47.7972	2.53100
In	19.1624	0.547600	18.5596	6.37760	4.29480	25.8499	2.03960	92.8029	4.93910

Table A.1: Coefficients for analytical approximation to the atomic scattering factors for relevant elements.

The second real quantity, f'_n , and the imaginary part, f''_n , are known as the anomalous scattering factors and account for resonance and absorption, respectively. For a given element these quantities may be found in the classic paper of Cromer and Liberman [147] for common X-ray tube wavelengths. The tables contain the results of relativistic calculations of the photoelectric cross-sections across the periodic table. Extensive tables of f' and f'' have also been calculated over larger energy ranges using the method of Brennan and Cowan [148]. It is interesting to note that the photoabsorption cross-section for an element may be written

$$\mu_0 = 2r_e \lambda f'' \quad . \quad (\text{A.6})$$

Figure A.2 shows the real and imaginary parts of the atomic form factors for the atoms relevant to both the diffraction and XAFS studies in this thesis. Note that the background absorption in XAFS measurements is related to the curves in the top of the figure. For a crystalline material, the mass absorption is given by

$$\mu_0 = \left(\frac{2\pi}{\lambda}\right) \Gamma F''_0 \quad , \quad (\text{A.7})$$

where the (000)-structure factor is written in terms of its real and imaginary parts as $F_0 = F'_0 + iF''_0$.

Figure A.2: The real and imaginary parts of the atomic form factors for Ga (heavy, solid lines), As (light, solid lines), and In (dashed lines). Abrupt changes are observed near the absorption edges, as indicated.

As an example, the structure factor for the GaAs (004)-reflection is calculated by taking the sum in Equation A.1 over the 4 Ga atoms and 4 As atoms in the unit cell. One obtains

$$F_H(004) = 4 \left[(f_{Ga}^0 + f'_{Ga} + i f''_{Ga}) + (f_{As}^0 + f'_{As} + i f''_{As}) \right] . \quad (\text{A.8})$$

Calculations of this type were used in the XSW data analysis described in Chapter 3.2.2. Thermal effects may be included by multiplying F_H by the Debye-Waller factor for the reflection, e^{-M} (see Section 3.2.2).

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