# The atomic structure of fluoride superlattices and antimonide surfaces

Thesis submitted for the degree of

Doctor of Philosophy

at the University of Leicester

by

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### The atomic structure of fluoride superlattices and antimonide surfaces

Simon Graham Alcock

#### Abstract

The atomic structure of the  $CaF_2$ -Si(111) interface and the repeated unit cell of  $MnF_2$ -CaF<sub>2</sub>-Si(111) superlattices have been determined using surface x-ray diffraction. Specular reflectivity and non-specular rod scans were measured for a number of superlattice samples. All samples had a type-B interface. Ultra-thin layers of  $MnF_2$ , below a critical thickness of 5 monolayers, adopted the fluorite structure of  $CaF_2$ . These layers are likely to have different magnetic properties to bulk anti-ferromagnetic  $MnF_2$ , possibly leading to novel magnetic applications. We have developed software to interface with the structure factor calculation software ROD to calculate the semi-kinematical reflectivity and non-specular rods of a superlattice.

Ion bombardment and annealing were used to produce atomically clean, well ordered InSb(001)- $c(4\times4)$  and GaSb(001)- $c(2\times6)$  surface reconstructions from antimony capped and uncapped samples. Auger electron spectroscopy showed that a 1000Å antimony capping layer was sufficient to prevent atmospheric oxidation of the substrate. A substantial re-ordering of the cap was observed at 180°C. Desorption of the cap was achieved by annealing the sample at 300°C under an Sb overpressure.

X-ray reflectivity measurements were used to determine the out-of-plane structure of the GaSb- $c(2\times 6)$  reconstruction. Theoretical fits indicate that both the top and the second layer of antimony dimers lie close to their bulk positions. In-plane x-ray measurements were used to verify the symmetry of the reconstruction.

The InSb anti-phase x-ray position was monitored during the growth of Tl on the InSb- $c(4\times 4)$  reconstruction. Fits to the data showed that the growth mode is Stranski–Krastanow at room temperature, and revealed details about the formation of the initial wetting layer. A specular reflectivity ridge scan after deposition showed reflections produced by Tl and Tl<sub>2</sub>O. In-plane x-ray diffraction peaks can be attributed to either Tl, TlSb, or Tl<sub>7</sub>Sb<sub>2</sub> and indicate a preferential alignment of Tl.

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# Chapter 1

# Introduction

## 1.1 Introduction

In recent years there has been a nanotechnology explosion! Not only are magnetic, electronic and optical devices becoming smaller, faster and more efficient, the different technologies are being integrated onto single substrates. The nanotechnology revolution is uniting the biological and physical sciences to measure, manipulate and understand matter at an atomic level. Many exciting ideas including: spintronic devices, where the intrinsic spin of the electron is exploited in addition to its charge; and quantum computing, where quantum interactions are used to perform logical operations, make the future bright for condensed matter physics. Advances in the growth of metals and semiconductors, using molecular beam epitaxial (MBE), has led to the production of complex, highly ordered structures. Coupled with this, scanning tunnelling microscopy (STM) and third generation sources of intense, coherent x-ray and UV synchrotron radiation offer in-situ, real-time measurement with sufficient temporal and spatial resolution to observe atomic and molecular reactions. A fundamental understanding of the atomic interactions and the dynamic topology of reconstructed semiconductor surfaces is essential for the production of nanoscale devices. This is especially critical for the growth of highly ordered ultrathin layers required for short-period superlattices and quantum well structures. For these reasons, there is a pressing need to understand the processes required to prepare atomically clean, highly ordered surface reconstructions.

In chapter 2 theoretical aspects of x-ray diffraction, Auger electron spectroscopy and co-ordinate transformation are introduced. The experimental equipment and techniques used to produce and characterise samples are summarised in chapter 3. In chapter 4 the atomic structure of the CaF<sub>2</sub>-Si(111) interface and the structure of ultra-thin MnF<sub>2</sub> films, contained within fluorite superlattices, are investigated. The production of atomically clean, well ordered InSb(001)-c(4×4) surface reconstructions and the growth of Tl on this surface is discussed in chapter 5. In chapter 6, the atomic structure of the GaSb(001)-c(2×6) surface reconstruction is determined. Finally, in chapter 7, a summary of the thesis is presented and suggestions for future work.

# Chapter 2

# Theoretical considerations

## 2.1 Introduction

In this chapter we derive the wave equation describing the full dynamical theory of xray diffraction and show how assuming negligible attenuation of the x-ray beam as it passes through the material leads to the simpler kinematical description of diffraction. Particular attention is paid to surface x-ray diffraction (SXRD) from a semi-infinite bulk crystal covered by reconstructed atomic layers. Auger electron spectroscopy (AES) is a useful surface sensitive probe used to determine the relative abundance of different atomic species at a sample surface. The basic theory of the underlying physical principles is discussed, to explain why the technique is surface sensitive and how quantitative chemical information can be extracted from the stream of detected electrons. Finally, we derive a general co-ordinate transformation matrix between any two frames of reference defined by non-orthonormal basis sets. This general transformation can be used in a number of crystallographic applications, including: the transformation between any real space crystal systems; and to convert between the real and reciprocal-space descriptions of x-ray scattering.

## 2.2 X-ray diffraction

#### 2.2.1 A brief history of x-ray diffraction

X-rays were discovered in 1895 by Wilhelm Röntgen during examination of the radiation produced during discharge from an electrode contained within an evacuated glass vessel (a Geisler discharge tube). It was soon realised that x-rays were electromagnetic waves with wavelengths comparable to interatomic distances. The energy, E of an x-ray photon is related to it's wavelength,  $\lambda$ , via:

$$E[\text{keV}] = \frac{hc}{1.602 \times 10^{-26} \times \lambda[\text{\AA}]} = \frac{12.409}{\lambda[\text{\AA}]}$$
(2.1)

In 1912 W. Friedrich, P. Knipping and M. von Laué obtained the first x-ray diffraction image of a crystal. The following year W. H and W. L Bragg examined diffracted x-rays from a number of crystals and formulated the Bragg equation, laying the foundations for x-ray crystallography:

$$n\lambda = 2d\sin\theta,\tag{2.2}$$

where *n* is the order of the reflection,  $\lambda$  is the wavelength of the x-ray radiation, *d* is the spacing between the scattering planes within the crystal, and  $\theta$  is the angle of incidence between the incident x-ray beam and the surface planes of the crystal. Geometric and dynamical theories were developed by C. G. Darwin in 1914 to predict the relative intensities of diffracted x-ray beams. His sophisticated dynamical theory decomposed the material into a number of thin slabs and used recurrence calculations to predict the transmission and reflection from each thin slab. In 1917, P. P. Ewald produced his own dynamical theory, in which the crystal was described by a periodic distribution of electric dipoles, each excited by the incident radiation. A different derivation and interpretation of Ewald's dynamical theory was given by M. von Laué in 1931. He showed that the interaction between the incident electromagnetic radiation and the crystal could be found by inserting a triply periodic function for the electric susceptibility into Maxwell's equations.

In the geometric (or kinematic) theory, the attenuation of the x-ray beam as it travels through the crystal is assumed to be negligible. This assumption considerably simplifies calculating the total diffracted intensity from a crystal.

#### 2.2.2 Maxwell's equations

To understand the diffraction of x-rays by matter, we must consider two factors: how x-rays scatter from individual atoms; and how all the scattered x-rays interfere with each other and the incident x-ray beam. Maxwell's equations describe the propagation of electric and magnetic fields ( $\mathbf{E}$  and  $\mathbf{H}$  respectively) and the electric (specified by the

electric displacement,  $\mathbf{D}$ ) and magnetic (specified by the magnetic induction,  $\mathbf{D}$ ) response of a material to the applied fields.

• Gauss' theorem applied to electrostatics ( $\rho_e$  is the charge density)

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = \rho_e(\mathbf{r}, t), \qquad (2.3)$$

• Gauss' theorem of magnetic fields

$$\nabla \cdot \mathbf{B}(\mathbf{r},t) = 0, \tag{2.4}$$

• Faraday and Lenz's law of electromagnetic induction

$$\nabla \wedge \mathbf{E}(\mathbf{r}, t) = \frac{-\partial \mathbf{B}(\mathbf{r}, t)}{\partial t},$$
(2.5)

• Ampere's law of magnetomotive forces ( $\sigma$  is the conductivity)

$$\nabla \wedge \mathbf{H}(\mathbf{r},t) = \sigma(\mathbf{r})\mathbf{E}(\mathbf{r},t) + \frac{\partial \mathbf{D}(\mathbf{r},t)}{\partial t},$$
(2.6)

The electric displacement vector,  $\mathbf{D}$ , is related to the applied electric field,  $\mathbf{E}$ , by the material's dielectric permittivity,  $\epsilon_r$ :

$$\mathbf{D}(\mathbf{r},t) = \epsilon_0 \epsilon_r(\mathbf{r}) \mathbf{E}(\mathbf{r},t), \qquad (2.7)$$

where  $\epsilon_0$  is the permittivity of free space. Analogously, the magnetic induction, **B**, is related to the applied magnetic field, **H**, by the material's magnetic permeability,  $\mu_r$ :

$$\mathbf{B}(\mathbf{r},t) = \mu_0 \mu_r(\mathbf{r}) \mathbf{H}(\mathbf{r},t), \qquad (2.8)$$

where  $\mu_0$  is the permeability of free space.

Alternately, the electric displacement,  $\mathbf{D}$ , can be described in terms of the incident electric field  $\mathbf{E}$  and a dipole polarisation density,  $\mathbf{P}$ , induced by the material as a reaction to the applied field:

$$\mathbf{D}(\mathbf{r},t) = \epsilon_0 \mathbf{E}(\mathbf{r},t) + \mathbf{P}(\mathbf{r},t).$$
(2.9)

In a dielectric medium, the polarisation density,  $\mathbf{P}$ , is proportional to the applied field  $\mathbf{E}$ ,

$$\mathbf{P}(\mathbf{r},t) = \chi_e(\mathbf{r})\epsilon_0 \mathbf{E}(\mathbf{r},t), \qquad (2.10)$$

where the constant of proportionality  $\chi_e$  is defined to be the electrical susceptibility (for simplification purposes, a factor of  $\epsilon_0$  is conventionally taken out of the constant of proportionality). Inserting the expression for **P**, given in equation 2.10, into equation 2.9 produces:

$$\mathbf{D}(\mathbf{r},t) = \epsilon_0 \mathbf{E}(\mathbf{r},t) + \chi_e(\mathbf{r})\epsilon_0 \mathbf{E}(\mathbf{r},t) = (1+\chi_e(\mathbf{r}))\epsilon_0 \mathbf{E}(\mathbf{r},t).$$
(2.11)

A comparison between equations 2.11 and 2.7 relates the electrical susceptibility,  $\chi_e$ , to the relative dielectric permittivity,  $\epsilon_r$ :

$$\epsilon_r(\mathbf{r}) = 1 + \chi_e(\mathbf{r}). \tag{2.12}$$

#### 2.2.3 Dynamical diffraction theory

We are now in a position to be able to solve Maxwell's equations to determine the spatial and temporal nature of the electric and magnetic fields.

#### Electromagnetic waves in a vacuum

Consider an electromagnetic wave propagating through free space:

$$\epsilon_r = 1, \mu_r = 1, \rho_e = 0$$
 and  $\sigma = 0.$  (2.13)

Under these conditions Maxwell's equations (equations 2.3, 2.4, 2.5 and 2.6) become:

$$\nabla \cdot \mathbf{E}(\mathbf{r},t) = 0, \qquad (2.14)$$

$$\nabla \cdot \mathbf{B}(\mathbf{r},t) = 0, \qquad (2.15)$$

$$\nabla \wedge \mathbf{E}(\mathbf{r}, t) = \frac{-\partial \mathbf{B}(\mathbf{r}, t)}{\partial t},$$
 (2.16)

$$\nabla \wedge \mathbf{B}(\mathbf{r}, t) = \mu_0 \epsilon_0 \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t}.$$
 (2.17)

A standard vector identity can be applied to the electric field:

$$\nabla \wedge (\nabla \wedge \mathbf{E}(\mathbf{r}, t)) = \nabla (\nabla \cdot \mathbf{E}(\mathbf{r}, t)) - \nabla^2 \mathbf{E}(\mathbf{r}, t).$$
(2.18)

Incorporating equations 2.14 and 2.16 into the vector identity produces:

$$\frac{\partial (\nabla \wedge \mathbf{B}(\mathbf{r}, t))}{\partial t} = \nabla^2 \mathbf{E}(\mathbf{r}, t).$$
(2.19)

Further simplification can be carried out by using equation 2.17:

$$\nabla^{2} \mathbf{E}(\mathbf{r}, t) = \mu_{0} \epsilon_{0} \frac{\partial^{2} \mathbf{E}(\mathbf{r}, t)}{\partial t^{2}} = \frac{1}{c^{2}} \frac{\partial^{2} \mathbf{E}(\mathbf{r}, t)}{\partial t^{2}}.$$
(2.20)

Equation 2.20 is the equation of propagation of an electromagnetic wave in vacuum. The simplest solution is a plane wave of the form:

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 e^{i(\omega t - \mathbf{k}_0 \cdot \mathbf{r})},\tag{2.21}$$

where the wavenumber  $k_0 (= 2\pi/\lambda)$  and the angular frequency  $\omega$  of the wave are related to the speed of light by:

$$c = \frac{\omega}{k_0} \tag{2.22}$$

#### Electromagnetic waves in a medium

Having determined the propagation equation for electromagnetic waves travelling through free space, our next task is to find an analogous expression for the electric displacement vector, **D**, within a material in response to the applied electric field. Von Laué's method assumes a continuous distribution of electrical charge throughout the medium. Since the crystal is electrically neutral, we can, to a first approximation, assume the local electric charge ( $\rho_e$ ) and the current density (related to the conductivity,  $\sigma$ ) to be zero. Under these conditions the general form of Maxwell's equations become:

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = 0 \tag{2.23}$$

$$\nabla \cdot \mathbf{B}(\mathbf{r},t) = 0 \tag{2.24}$$

$$\nabla \wedge \mathbf{E}(\mathbf{r}, t) = -\mu_0 \frac{\partial \mathbf{H}(\mathbf{r}, t)}{\partial t}$$
 (2.25)

$$\nabla \wedge \mathbf{H}(\mathbf{r}, t) = \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t}.$$
 (2.26)

Note that while  $\nabla \cdot \mathbf{D}$  is equal to zero, this isn't generally true for  $\nabla \cdot \mathbf{E}$ . The electric displacement,  $\mathbf{D}$ , is the most suitable quantity to describe the distorted electric field within the medium. The propagation equation for electromagnetic waves within the medium can now be found by applying the vector operator ( $\nabla \wedge$ ) to both sides of equation 2.25, and substitute this into equation 2.26:

$$\nabla \wedge (\nabla \wedge \mathbf{E}(\mathbf{r}, t)) = -\mu_0 \frac{\partial}{\partial t} \left( \nabla \wedge \mathbf{H}(\mathbf{r}, t) \right) = -\mu_0 \frac{\partial^2 \mathbf{D}(\mathbf{r}, t)}{\partial t^2}.$$
 (2.27)

From equations 2.7 and 2.12:

$$\epsilon_0 \mathbf{E}(\mathbf{r}, t) = \frac{\mathbf{D}(\mathbf{r}, t)}{(1 + \chi_e(\mathbf{r}))} \approx \mathbf{D}(\mathbf{r}, t) (1 - \chi_e(\mathbf{r})) \approx \mathbf{D}(\mathbf{r}, t) - \chi_e(\mathbf{r})\mathbf{D}(\mathbf{r}, t), \qquad (2.28)$$

where the binomial theory has been used to expand the denominator (this is a valid approximation as  $\chi_e$  is typically of the order  $10^{-5}$  which is much smaller than unity). This expression for  $\mathbf{E}(\mathbf{r}, t)$  can be substituted into equation 2.27 to produce a wave equation for the electric displacement field:

$$\nabla \wedge (\nabla \wedge (\mathbf{D}(\mathbf{r},t) - \mathbf{D}(\mathbf{r},t)\chi_e(\mathbf{r}))) = -\epsilon_0 \mu_0 \frac{\partial^2 \mathbf{D}(\mathbf{r},t)}{\partial t^2}$$
(2.29)

$$\nabla \wedge (\nabla \wedge \mathbf{D}(\mathbf{r}, t)) - \nabla \wedge (\nabla \wedge (\chi_e(\mathbf{r})\mathbf{D})) = -\frac{1}{c^2} \frac{\partial^2 \mathbf{D}(\mathbf{r}, t)}{\partial t^2}.$$
 (2.30)

Since the temporal and spatial characteristics of the displacement field can be separated, we can calculate the partial differential with respect to time:

Use this expression for the partial differential of the electric displacement and expanding  $\nabla \wedge (\nabla \wedge (\mathbf{D}(\mathbf{r}, t)))$  using the vector identity in equation 2.18, equation 2.30 becomes:

$$\nabla(\nabla \cdot \mathbf{D}(\mathbf{r},t)) - \nabla^2 \mathbf{D}(\mathbf{r},t) - \nabla \wedge (\nabla \wedge (\chi_e(\mathbf{r})\mathbf{D}(\mathbf{r},t))) = \frac{\omega^2}{c^2}\mathbf{D}(\mathbf{r},t).$$
(2.32)

Finally, making use of equations 2.22 and 2.23 and cancelling out the time dependence, we have an expression for the propagation of electromagnetic waves travelling through a medium:

$$\nabla^{2}\mathbf{D}(\mathbf{r}) + \nabla \wedge (\nabla \wedge (\chi_{e}(\mathbf{r})\mathbf{D}(\mathbf{r}))) + k_{0}^{2}\mathbf{D}(\mathbf{r}) = 0.$$
(2.33)

The solutions of this propagation equation form the basis of the dynamical theory of diffraction [1–4].

# 2.2.4 The classical interaction of electromagnetic radiation with charged particles

To be able to solve the wave equation, given by equation 2.33, we need to find an expression for the electrical susceptibility,  $\chi_e(\mathbf{r})$  by considering the electromagnetic forces acting upon a single electron.

#### The Lorentz force

Charged particles experience the Lorentz force when placed in an electromagnetic field:

$$\mathbf{F}_{Lorentz} = m \frac{d^2 \mathbf{r}(t)}{dt^2} = q(\mathbf{E} + \mathbf{v} \wedge \mathbf{B})$$
(2.34)

where m and q are the particle's mass and charge respectively. Using the fact that

$$\mathbf{B} = \frac{1}{c} (\hat{\mathbf{k}} \wedge \mathbf{E}), \qquad (2.35)$$

where  $\hat{\mathbf{k}}$  is a unit vector in the incident electromagnetic waves direction, we can rewrite equation 2.34 as

$$m\frac{d^{2}\mathbf{r}(t)}{dt^{2}} = q(\mathbf{E} + \frac{\mathbf{v}}{c} \wedge (\hat{\mathbf{k}} \wedge \mathbf{E})).$$
(2.36)

The maximum value of  $\mathbf{k} \wedge \mathbf{E}$  is equal to the magnitude of the electric field vector,  $|\mathbf{E}|$ and therefore the maximum value of the magnetic interaction term in equation 2.34 is vE/c. In the Bohr model of a one-electron atom, the speed of an electron in an orbit with principal quantum number n around a nucleus with an atomic number Z is equal to

$$v = \frac{Zq^2}{4\pi\epsilon_0\hbar n} \approx \frac{Zc}{137n} \tag{2.37}$$

This shows that for light atoms, the ratio of v/c is small and hence the magnetic term in the Lorentz force can be neglected.

$$m \frac{d^2 \mathbf{r}(t)}{dt^2} \approx q \mathbf{E}.$$
 (2.38)

#### Scattering mechanisms

There are two main forms of scattering:

- Elastic scattering. All the energy transferred from the incident photon to a free electron (Thomson scattering) or to a partially bound electron (resonant or anomalous scattering) is re-radiated. Elastically scattered photons add coherently and give rise to diffraction effects and intense Bragg peaks.
- Inelastic (Compton) scattering. The incident photon transfers kinetic energy to the electron, lowering the energy of the scattered photon. Inelastically scattered photons give rise to a smoothly varying background, which often needs to be subtracted during x-ray experiments.

#### Resonant (anomalous) and Thomson scattering

The equation of motion for a partly bound electron, perturbed by the applied electric field to a displacement of  $\Delta \mathbf{r}_e(t)$  from its equilibrium position,  $\mathbf{r}_e$ , is:

$$\sum \mathbf{F} = q \mathbf{E}(\mathbf{r}_e + \Delta \mathbf{r}_e, t) - g \frac{d\Delta \mathbf{r}_e(t)}{dt} - h\Delta \mathbf{r}_e = m \frac{d^2 \Delta \mathbf{r}_e(t)}{dt^2}$$
(2.39)

where a damping force proportional to the charged particle's velocity and a restoring force have been included. Equation 2.21 shows that a plane-wave electric field can be separated into its spatial and temporal components:

$$\mathbf{E}(\mathbf{r}_e, t) = \mathbf{E}_0 e^{-i\mathbf{k}_0 \cdot \mathbf{r}_e} e^{i\omega t} = \mathbf{E}(\mathbf{r}_e)\mathbf{E}(t).$$
(2.40)

If we assume that the electric field strength is spatially constant over the charged particles oscillation range  $(\mathbf{E}(\mathbf{r}_e + \Delta \mathbf{r}_e) = \mathbf{E}(\mathbf{r}_e) = \mathbf{E}_0)$ , then:

$$\mathbf{E}(\mathbf{r}_e + \Delta \mathbf{r}_e, t) = \mathbf{E}(\mathbf{r}_e + \Delta \mathbf{r}_e)\mathbf{E}(t) = \mathbf{E}_0\mathbf{E}(t) = \mathbf{E}_0e^{i\omega t}.$$
 (2.41)

Substitution of equation 2.41 into equation 2.39 leads to:

$$m\frac{d^2\Delta \mathbf{r}_e(t)}{dt^2} + g\frac{d\Delta \mathbf{r}_e(t)}{dt} + h\Delta \mathbf{r}_e = q\mathbf{E}_0 e^{i\omega t}.$$
(2.42)

This second order differential equation (D.E) has the solution:

$$\Delta \mathbf{r}_{e}(t) = A e^{(\frac{-g + \sqrt{g^{2} - 4mh}}{2m})t} + B e^{(\frac{-g - \sqrt{g^{2} - 4mh}}{2m})t} + \frac{q \mathbf{E}_{0}(h - m\omega^{2} - ig\omega)e^{i\omega t}}{(h - m\omega^{2})^{2} + g^{2}\omega^{2}}.$$
 (2.43)

Since the first two terms in the solution have negative exponentials (which will decrease with time), the steady state solution of this equation (as  $t \to \infty$ ) is:

$$\Delta \mathbf{r}_e(t) = \frac{q \mathbf{E}_0 (h - m\omega^2 - ig\omega) e^{i\omega t}}{(h - m\omega^2)^2 + g^2 \omega^2}.$$
(2.44)

For non-zero values of h, resonance occurs when  $\omega = \omega_0$  giving  $h = m\omega_0^2$ , therefore:

$$\Delta \mathbf{r}_e(t) = \frac{q \mathbf{E}_0(m\omega_0^2 - m\omega^2 - ig\omega)e^{i\omega t}}{(m\omega_0^2 - m\omega^2)^2 + g^2\omega^2}.$$
(2.45)

For Thomson scattering we assume scattering from a free electron g = h = 0, and equation 2.45 reduces to:

$$\Delta \mathbf{r}_e(t) = -\frac{q_e \mathbf{E}_0 e^{i\omega t}}{m_e \omega^2} = \frac{q_e \mathbf{E}_0 e^{i(\omega t - \pi)}}{m_e \omega^2}.$$
(2.46)

Note that there is a phase difference of  $\pi$  radians between the incident wave and the motion of the electron and the outgoing wave.

#### Calculating the electrical susceptibility, $\chi_e$

The instantaneous dipole moment produced by the displacement of an electron is:

$$\mathbf{p} = q_e \Delta \mathbf{r}_e \tag{2.47}$$

The total polarisation,  $\mathbf{P}$ , contained within a volume V is proportional to the vector sum of all the microscopic moments  $\mathbf{p}_i$ :

$$\mathbf{P}(\mathbf{r},t) = \frac{1}{V} \sum \mathbf{p}_i = \frac{-q_e}{V} \sum \Delta \mathbf{r}_e$$
(2.48)

For our system, which has electron number density  $\rho(\mathbf{r})$ , the total polarisation is:

$$\mathbf{P}(\mathbf{r},t) = -q_e \rho(\mathbf{r}) \Delta \mathbf{r}_e(t) = \frac{-q_e^2 \rho(\mathbf{r})}{m_e \omega^2} \mathbf{E}(\mathbf{r}) e^{i\omega t}.$$
(2.49)

Comparison between equations 2.10 and 2.49 shows that the electrical susceptibility,  $\chi_e$ , is proportional to the electron density,  $\rho(\mathbf{r})$ , within the material:

$$\chi_{e} = \frac{-q_{e}^{2}\rho(\mathbf{r})}{m_{e}\epsilon_{0}\omega^{2}} = \frac{-4\pi r_{0}c^{2}}{\omega^{2}}\rho(\mathbf{r}) = \frac{-r_{0}\lambda^{2}\rho(\mathbf{r})}{\pi},$$
(2.50)

where  $\lambda$  is the wavelength of the electromagnetic wave and  $r_0$  is the classical radius of the electron ( $r_0 = 2.818 \times 10^{-15}$  m):

$$r_0 = \frac{q_e^2}{4\pi \ \epsilon_0 m_e c^2}.$$
 (2.51)

The electrical susceptibility is always negative and very small (typically of the order of  $10^{-6}$ ). The importance of equation 2.50 is that given an expression for the electron density within the material we can calculate the electrical susceptibility and solve the propagation equation 2.33.

#### 2.2.5 Kinematical diffraction theory

Kinematic diffraction theory [5–7] is an approximation to the full dynamical theory. The attenuation of the beam as it travels through the crystal is neglected. This assumption is

justified by the weak interaction of the radiation field with the crystal, and is valid in all cases except at certain angles of incidence (Bragg angles) where a significant percentage of the radiation is diffracted by the crystal. Assuming a constant electromagnetic amplitude throughout the medium means that the radiation scattered by each electron is identical. The total diffracted intensity is calculated by simply adding the radiation scattered by each electron, taking into account the geometrical phase differences.

To derive the kinematic approximation from the full dynamical theory we approximate each of the terms in the dynamical propagation equation 2.33:

$$\underbrace{\nabla^2 \mathbf{D}(\mathbf{r})}_1 + \underbrace{\nabla \wedge (\nabla \wedge (\chi_e(\mathbf{r})\mathbf{D}(\mathbf{r})))}_2 + \underbrace{k_0^2 \mathbf{D}(\mathbf{r})}_3 = 0$$
(2.52)

#### Term 1

If we assume that the spatial periodicity of the electrical susceptibility,  $\chi_e$ , is much larger than that of the electromagnetic field within the medium we can approximate  $\nabla^2 \chi_e$  to zero, therefore:

$$\nabla^{2} \mathbf{D}(\mathbf{r}) = \epsilon_{0} \epsilon_{r} \nabla^{2} \mathbf{E}(\mathbf{r}) + \epsilon_{0} \mathbf{E}(\mathbf{r}) \nabla^{2} \chi_{e} \approx \epsilon_{0} \epsilon_{r} \nabla^{2} \mathbf{E}(\mathbf{r})$$
(2.53)

#### Term 2

Using the same assumption that  $\chi_e$  is approximately independent of position:

$$\nabla \wedge (\nabla \wedge (\chi_{e}(\mathbf{r})\mathbf{D}(\mathbf{r}))) \approx \chi_{e}(\mathbf{r})\nabla \wedge (\nabla \wedge \mathbf{D}(\mathbf{r}))$$
$$\approx \chi_{e}(\mathbf{r})\epsilon_{0}\nabla \wedge (\nabla \wedge \mathbf{E}(\mathbf{r}))$$
$$\approx \chi_{e}(\mathbf{r})\epsilon_{0}\epsilon_{r}k_{0}^{2}\mathbf{E}(\mathbf{r}) \qquad (2.54)$$

#### Term 3

Substituting an expression for the displacement vector in terms of the applied field:

$$k_0^2 \mathbf{D}(\mathbf{r}) = k_0^2 \epsilon_0 \epsilon_r \mathbf{E}(\mathbf{r}) \tag{2.55}$$

The approximations in equations 2.53, 2.54 and 2.55 can now be substituted into the exact dynamical propagation equation (equation 2.33):

$$\epsilon_0 \epsilon_r \nabla^2 \mathbf{E}(\mathbf{r}) + \chi_e(\mathbf{r}) k_0^2 \epsilon_0 \epsilon_r \mathbf{E}(\mathbf{r}) + k_0^2 \epsilon_0 \epsilon_r \mathbf{E}(\mathbf{r}) = 0$$
(2.56)

We can now re-arrange equation 2.56 and insert the expression for the electrical susceptibility (equation 2.50), to form the approximated kinematic propagation equation:

$$\left(\nabla^2 + k_0^2 - 4\pi r_0 \rho(\mathbf{r})\right) \mathbf{E}(\mathbf{r}) = 0.$$
(2.57)

# 2.2.6 The solution of the kinematic propagation equation for a periodic electron distribution function, $\rho(\mathbf{r})$

We now have an expression for the kinematical propagation equation (equation 2.57). The next step is to find an expression for the electron distribution function,  $\rho(\mathbf{r})$ , within a crystal. A crystal structure is constructed by convolving the crystal lattice and the basis function. The basis represents the arrangement of atoms contained within a volume known as the unit cell. The crystal structure is formed by placing a unit cell at every lattice point. Consider an electron which orbits the *j*th atom in the *n*th unit cell (see figure 2.1). Its position,  $\mathbf{r}_e$ , relative to the origin of the crystal lattice is:

$$\mathbf{r}_e = \mathbf{R}_n + \mathbf{r}_j + \mathbf{r}',\tag{2.58}$$

where  $\mathbf{R}_n$ , represents the position of the origin of the nth unit cell relative to the crystal lattice origin;  $\mathbf{r}_j$  represents the position of the jth atom relative to the origin of the unit

cell; and  $\mathbf{r}'$  represents the position of an electron relative to the jth nucleus within the unit cell. Let a general position within the medium be  $\mathbf{r}$  and a detector be located at  $\mathbf{R}_0$  (see figure 2.1).

The kinematic propagation equation (equation 2.57) can be re-written as:

$$\left(\nabla^2 + k_0^2\right) \mathbf{E}(\mathbf{r}) = 4\pi r_e \rho(\mathbf{r}) \mathbf{E}(\mathbf{r}).$$
(2.59)

The general solution of this second order differential equation is the sum of two parts: the complementary function (C.F); and the particular integral (P.I):

$$\mathbf{E} = \mathbf{E}_{C.F} + \mathbf{E}_{P.I}.\tag{2.60}$$

#### The complementary function

The complementary function satisfies:

$$\left(\nabla^2 + k_0^2\right) \mathbf{E}_{C.F}(\mathbf{r}) = 0.$$
 (2.61)

Comparison with equation 2.59 shows that the complementary function represents the solution of the fundamental wave equation as the electron density within the medium tends to zero ( $\rho(\mathbf{r}) \rightarrow 0$ ). Since electrons are the primary scatterers of electromagnetic radiation, the complementary function can be thought of as the incident wave travelling through a vacuum. The solution to equation 2.61 is simply:

$$\mathbf{E}_{C.F}(\mathbf{r}) = \mathbf{E}_0 e^{-i\mathbf{k}_0 \cdot \mathbf{r}}.$$
(2.62)

#### The particular integral

If a Green's function  $G(\mathbf{R}_0, \mathbf{r}_e)$  exists which satisfies

$$(\nabla_{\mathbf{R}}^2 + k_0^2)G(\mathbf{R}_0, \mathbf{r}_e) = \delta(\mathbf{R}_0, \mathbf{r}_e), \qquad (2.63)$$



Figure 2.1: The location of an electron belonging to the *j*th atom in the *n*th unit cell, relative to the crystal origin (top diagram) and the reciprocal space representations of a scattering process, showing the incident wavevector  $\mathbf{k}_0$ , the outgoing wavevector  $\mathbf{k}_f$  and the change in momentum (bottom diagram)

where  $\nabla_{\mathbf{R}}^2$  indicates differentiation with respect to  $\mathbf{R}_0$  (as opposed to  $\mathbf{r}_e$ ), then the Green's function method predicts that the particular integral component of the general solution to the fundamental wave equation is:

$$\mathbf{E}_{P.I}(\mathbf{R}_0) = \int G(\mathbf{R}_0, \mathbf{r}_e) 4\pi r_0 \rho(\mathbf{r}_e) \mathbf{E}(\mathbf{r}_e) d\mathbf{r}_e.$$
 (2.64)

This mathematical result is readily understood in physical terms. Equation 2.63 describes the scattered wave produced by a point source located at  $\mathbf{r}_e$ . If several scattering centres exist within the medium, kinematical theory predicts that the total scattered wave will be equal to the sum of the amplitudes of the incident wave and the waves produced by each individual scatterer. The value of  $\mathbf{E}(\mathbf{r})$  in equation 2.59 represents the total wave at a general position,  $\mathbf{r}$ , within the medium. A Green's function which satisfies equation 2.63 is:

$$G(\mathbf{R}_0, \mathbf{r}_e) = -\frac{1}{4\pi} \frac{e^{-i|\mathbf{k}_0||\mathbf{R}_0 - \mathbf{r}_e|}}{|\mathbf{R}_0 - \mathbf{r}_e|}.$$
(2.65)

#### Proof that the Green's function satisfies equation 2.63

To prove that equation 2.65 does satisfy 2.63 we can make use of a standard integral:

$$-\frac{1}{4\pi} \frac{e^{-i|\mathbf{k}_0||\mathbf{R}_0 - \mathbf{r}_e|}}{|\mathbf{R}_0 - \mathbf{r}_e|} = \lim_{\Omega \to 0} \frac{1}{8\pi^3} \int \frac{e^{-i\mathbf{v} \cdot (\mathbf{R}_0 - \mathbf{r}_e)}}{k_0^2 - v^2 + i\Omega} d\mathbf{v}$$
(2.66)

and substitute this form for the Green's function back into equation 2.63 and simplify:

$$(\nabla_{r}^{2} + k_{0}^{2})G(\mathbf{R}_{0}, \mathbf{r}_{e}) = (\nabla_{\mathbf{R}}^{2} + k_{0}^{2}) \lim_{\Omega \to 0} \frac{1}{8\pi^{3}} \int \frac{e^{-i\mathbf{v} \cdot (\mathbf{R}_{0} - \mathbf{r}_{e})}}{k_{0}^{2} - v^{2} + i\Omega} d\mathbf{q}$$

$$= \lim_{\Omega \to 0} \frac{1}{8\pi^{3}} \int \frac{\nabla_{r}^{2} e^{i\mathbf{v} \cdot (\mathbf{R}_{0} - \mathbf{r}_{e})} + k_{0}^{2} e^{i\mathbf{v} \cdot (\mathbf{R}_{0} - \mathbf{r}_{e})}}{k_{0}^{2} - v^{2} + i\Omega} d\mathbf{v}$$

$$= \lim_{\Omega \to 0} \frac{1}{8\pi^{3}} \int \frac{(k_{0}^{2} - v^{2}) e^{-i\mathbf{v} \cdot (\mathbf{R}_{0} - \mathbf{r}_{e})}}{k_{0}^{2} - v^{2} + i\Omega} d\mathbf{v}$$

$$\approx \frac{1}{8\pi^{3}} \int e^{-i\mathbf{v} \cdot (\mathbf{R}_{0} - \mathbf{r}_{e})} d\mathbf{v} = \delta(\mathbf{R}_{0}, \mathbf{r}_{e}).$$

$$(2.67)$$

The general solution to equation 2.59 can now be stated:

$$\mathbf{E}(\mathbf{R}_0) = \mathbf{E}_0 e^{-i\mathbf{k}_0 \cdot \mathbf{R}_0} - r_e \int \frac{\rho(\mathbf{r}_e) \mathbf{E}(\mathbf{r}_e) e^{-i|\mathbf{k}_0||\mathbf{R}_0 - \mathbf{r}_e|} d\mathbf{r}_e}{|\mathbf{R}_0 - \mathbf{r}_e|}.$$
 (2.68)

#### The asymptotic form of the Green function

We now have an exact formula for the Green's function (equation 2.65). To help simplify the Green's function, a number of approximations can be made by considering the system's geometry (see figure 2.1),

$$|\mathbf{R}_{0} - \mathbf{r}_{e}|^{2} = |\mathbf{R}_{0}|^{2} + |\mathbf{r}_{e}|^{2} - 2 |\mathbf{R}_{0}| |\mathbf{r}_{e}| \cos \alpha$$
  

$$|\mathbf{R}_{0} - \mathbf{r}_{e}| = \sqrt{|\mathbf{R}_{0}|^{2} + |\mathbf{r}_{e}|^{2} - 2 |\mathbf{R}_{0}| |\mathbf{r}_{e}| \cos \alpha}$$
  

$$= |\mathbf{R}_{0}| \sqrt{1 + \frac{|\mathbf{r}_{e}|^{2}}{|\mathbf{R}_{0}|^{2}} - \frac{2|\mathbf{r}_{e}|}{|\mathbf{R}_{0}|} \cos \alpha}, \qquad (2.69)$$

where  $\alpha$  is the angle between  $\mathbf{R}_0$  and  $\mathbf{r}_e$ . Since  $|\mathbf{R}_0| \gg |\mathbf{r}_e|$ , we can neglect the second term contained within the square root and expand the resulting expression using the Binomial theory:

$$|\mathbf{R}_{0} - \mathbf{r}_{e}| \approx |\mathbf{R}_{0}| \sqrt{1 - \frac{2|\mathbf{r}_{e}|}{|\mathbf{R}_{0}|} \cos \alpha}$$
$$\approx |\mathbf{R}_{0}| \left(1 - \frac{|\mathbf{r}_{e}|}{|\mathbf{R}_{0}|} \cos \alpha\right)$$
$$\approx |\mathbf{R}_{0}| - |\mathbf{r}_{e}| \cos \alpha. \qquad (2.70)$$

The asymptotic form of the Green's function becomes:

$$G(\mathbf{R}_{0}, \mathbf{r}_{e}) = -\frac{1}{4\pi} \frac{e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0} - \mathbf{r}_{e}|}}{|\mathbf{R}_{0} - \mathbf{r}_{e}|}$$

$$\approx -\frac{1}{4\pi} \frac{e^{-i|\mathbf{k}_{0}|(|\mathbf{R}_{0}| - |\mathbf{r}_{e}|\cos\alpha)}}{|\mathbf{R}_{0}|}$$

$$\approx -\frac{1}{4\pi} \frac{e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}e^{i|\mathbf{k}_{0}||\mathbf{r}_{e}|\cos\alpha}}{|\mathbf{R}_{0}|}.$$
(2.71)

#### The asymptotic form of the general solution

If we incorporate the asymptotic form of the Green's function (equation 2.71) into the general solution (equation 2.68) we obtain the asymptotic form of the general solution:

$$\mathbf{E}(\mathbf{R}_0) \approx \mathbf{E}_0 e^{-i\mathbf{k}_0 \cdot \mathbf{R}_0} - r_0 \int \frac{\rho(\mathbf{r}_e) \mathbf{E}(\mathbf{r}_e) e^{-i|\mathbf{k}_0||\mathbf{R}_0|} e^{i|\mathbf{k}_0||\mathbf{r}_e|\cos\alpha} d\mathbf{r}_e}{|\mathbf{R}_0|}.$$
 (2.72)

#### 2.2.7 The Born approximation

Since the strength of the electric field at the detector,  $\mathbf{E}(\mathbf{R}_0)$ , in equation 2.72 depends upon the value of  $\mathbf{E}$  at all other locations in space (denoted by  $\mathbf{E}(\mathbf{r}_e)$ ) we cannot determine  $\mathbf{E}(\mathbf{R}_0)$  explicitly. Instead, a successive approximation procedure is required. In the zeroth order Born approximation ( $\mathbf{E}^n$  denotes the nth Born approximation) we totally neglect the scattered part of the wave:

$$\mathbf{E}^{0}(\mathbf{R}_{0}) \approx \mathbf{E}_{0} e^{-i\mathbf{k}_{0} \cdot \mathbf{R}_{0}},\tag{2.73}$$

The next step is to substitute this expression into equation 2.72 to get the asymptotic form of the first order Born approximation:

$$\mathbf{E}^{1}(\mathbf{R}_{0}) \approx \mathbf{E}_{0}e^{-i\mathbf{k}_{0}\cdot\mathbf{R}_{0}} - r_{0}\int \frac{\rho(\mathbf{r}_{e})\mathbf{E}^{0}(\mathbf{r}_{e})e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}e^{i|\mathbf{k}_{0}||\mathbf{r}_{e}|\cos\alpha}d\mathbf{r}_{e}}{|\mathbf{R}_{0}|} \\
\approx \mathbf{E}_{0}e^{-i\mathbf{k}_{0}\cdot\mathbf{R}_{0}} - r_{0}\int \frac{\rho(\mathbf{r}_{e})\mathbf{E}_{0}e^{-i\mathbf{k}_{0}\cdot\mathbf{r}_{e}}e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}e^{i|\mathbf{k}_{0}||\mathbf{r}_{e}|\cos\alpha}d\mathbf{r}_{e}}{|\mathbf{R}_{0}|} \\
\approx \mathbf{E}_{0}e^{-i\mathbf{k}_{0}\cdot\mathbf{R}_{0}} - \frac{r_{0}\mathbf{E}_{0}e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}}{|\mathbf{R}_{0}|}\int \rho(\mathbf{r}_{e})e^{-i\mathbf{k}_{0}\cdot\mathbf{r}_{e}}e^{i|\mathbf{k}_{0}||\mathbf{r}_{e}|\cos\alpha}d\mathbf{r}_{e}. \quad (2.74)$$

Clearly, this procedure could be used to find the higher order Born approximations. We define the scattered wavevector,  $\mathbf{k}_f$ , to be a vector of length  $|\mathbf{k}_0|$  (elastic scattering), in the direction from the crystallographic origin towards the detector (see figure 2.1):

$$\mathbf{k}_f = \mid \mathbf{k}_0 \mid \hat{\mathbf{R}}_0. \tag{2.75}$$

We now take the dot product of  $\mathbf{k}_f$  with  $\mathbf{r}_e$ :

$$\mathbf{k}_f \cdot \mathbf{r}_e = |\mathbf{k}_0| \, \hat{\mathbf{R}}_0 \cdot \mathbf{r}_e = |\mathbf{k}_0| |\mathbf{r}_e| \cos \alpha.$$
(2.76)

This expression can be inserted into the first Born approximation (equation 2.74) to give (only considering the total scattered wave,  $\mathbf{E}_{S}(\mathbf{R}_{0})$ ) an expression for the total scattered field,  $\mathbf{E}_S$ :

$$\mathbf{E}_{S}(\mathbf{R}_{0}) = \mathbf{E}_{P.I}(\mathbf{R}_{0}) \approx \frac{-r_{0}\mathbf{E}_{0}e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}}{|\mathbf{R}_{0}|} \int \rho(\mathbf{r}_{e})e^{-i\mathbf{k}_{0}\cdot\mathbf{r}_{e}}e^{i\mathbf{k}_{f}\cdot\mathbf{r}_{e}}d\mathbf{r}_{e}$$

$$\approx \frac{-r_{0}\mathbf{E}_{0}e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}}{|\mathbf{R}_{0}|} \int \rho(\mathbf{r}_{e})e^{i(\mathbf{k}_{f}-\mathbf{k}_{0})\cdot\mathbf{r}_{e}}d\mathbf{r}_{e}$$

$$\approx \frac{-r_{0}\mathbf{E}_{0}e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}}{|\mathbf{R}_{0}|} \int \rho(\mathbf{r}_{e})e^{i\mathbf{q}\cdot\mathbf{r}_{e}}d\mathbf{r}_{e} \qquad (2.77)$$

where we have defined  $\mathbf{q}(=\mathbf{k}_f - \mathbf{k}_0)$  to be the "momentum transfer" (strictly speaking, the momentum of the wave is  $\hbar k$ ).

### 2.2.8 The electronic distribution, $\rho(\mathbf{r})$ , in an array of unit cells

In the case of an array of unit cells, we have an explicit periodic expression for the location of each electron,  $\mathbf{r}_e$  (see figure 2.1), and can easily evaluate the integral term in equation 2.77 by summing over the *J* electrons contained in each of the *N* unit cells:

$$\int \rho(\mathbf{r}_{e})e^{i\mathbf{q}\cdot\mathbf{r}_{e}}d\mathbf{r}_{e} = \sum_{n=1}^{n=N}\sum_{j=1}^{j=J}\int \rho(\mathbf{r}')e^{i\mathbf{q}\cdot(\mathbf{R}_{n}+\mathbf{r}_{j}+\mathbf{r}')}d\mathbf{r}'$$

$$= \sum_{n=1}^{n=N}\sum_{j=1}^{j=J}e^{i\mathbf{q}\cdot(\mathbf{R}_{n}+\mathbf{r}_{j})}\int \rho(\mathbf{r}')e^{i\mathbf{q}\cdot\mathbf{r}'}d\mathbf{r}'$$

$$= \sum_{n=1}^{n=N}e^{i\mathbf{q}\cdot\mathbf{R}_{n}}(\sum_{j=1}^{j=J}f_{j}(q)e^{i\mathbf{q}\cdot\mathbf{r}_{j}})$$

$$= F(\mathbf{q})\sum_{n=1}^{n=N}e^{i\mathbf{q}\cdot\mathbf{R}_{n}}.$$
(2.78)

The following definitions were used to derive the final format of equation 2.78:

1. The atomic form factor (or the atomic scattering factor),  $f_j(q)$ , is defined as

$$f_j(q) = \int \rho(\mathbf{r}') e^{i\mathbf{q}\cdot\mathbf{r}'} d\mathbf{r}'.$$
(2.79)

This represents the scattering from all the electrons belonging to the jth atom of the unit cell (a full quantum mechanical treatment produces an identical result [8]). The

atomic form factor depends primarily upon the magnitude of the momentum transfer and is approximately independent of the direction of  $\mathbf{q}$  due to the approximate spherical symmetry of atoms. In practise, there are wavelength dependent changes to the amplitude and phase of the scattering due to dispersion and resonance. To account for these factors, the atomic form factor is a complex quantity (real and imaginary components):

$$f(q) = f^{0}(q) + f'(q) + if''(q), \qquad (2.80)$$

where  $f^{0}(q)$  is the kinematical atomic form factor and f'(q) and f''(q) are the real and imaginary dispersion corrections respectively. Tabulated values of the atomic form factor, for all the elements, are listed online <sup>1</sup> and in reference [9], a copy of which can be obtained on-line <sup>2</sup>.

2. The structure factor,  $F(\mathbf{q})$ , is defined as:

$$F(\mathbf{q}) = \sum_{j=1}^{j=J} f_j(q) e^{i\mathbf{q}\cdot\mathbf{r}_j}.$$
(2.81)

This represents the scattering from all the atoms contained within the unit cell. Unlike  $f_j(q)$ , the structure factor depends upon the direction of the momentum transfer vector **q** since the relative positions of the atoms within the unit cell are important. An alternate, equivalent definition of the structure factor can be found by assuming a continuous form for the electron density within the unit cell:

$$F(\mathbf{q}) = \int \rho(\mathbf{D}) e^{i\mathbf{q}\cdot\mathbf{D}} d\mathbf{D}.$$
 (2.82)

Note that in this definition, the structure factor is the Fourier transform of the electron density within the unit cell. If the structure factor can be deduced from x-ray diffraction experiments, the electron density and hence the atomic arrangement within the unit cell (as the electron density peaks strongly at atomic sites) can be calculated by taking the inverse Fourier transform of the experimental structure

<sup>&</sup>lt;sup>1</sup>http://www-cxro.lbl.gov/optical\_contents/asf.html <sup>2</sup>http://www-cxro.lbl.gov/data\_booklet

factors. If the origin of the unit cell coincides with a centre of symmetry (e.g for every atom located at position  $\mathbf{r}_j$  there is an identical atom at position  $-\mathbf{r}_j$ ), then the structure factor simplifies to:

$$F(\mathbf{q}) = 2 \sum_{j=1}^{j=J/2} f_j(q) \cos\left(\mathbf{q} \cdot \mathbf{r}_j\right).$$
(2.83)

We can now combine equations 2.77 and 2.78 to produce an expression for the total scattered field of N unit cells, each having a structure factor  $F(\mathbf{q})$  in the first Born approximation:

$$\mathbf{E}_{S}^{1}(\mathbf{R}_{0}) \approx \frac{-r_{0}\mathbf{E}_{0}e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}}{|\mathbf{R}_{0}|}F(\mathbf{q})\sum_{n=1}^{n=N}e^{i\mathbf{q}\cdot\mathbf{R}_{n}}$$
(2.84)

#### 2.2.9 The Debye-Waller factor

In our previous derivations, we assumed each atom to be located exactly at its equilibrium position. In reality, each atom will be randomly displaced from its mean position by a number of factors including thermal motion. These displacements may be of appreciable size but the time period of these thermal oscillations is very long compared to the time taken for the x-rays to travel through the material. To a good approximation we can therefore consider each atom to be stationary at a random displacement  $\Delta \mathbf{r}_j$  from its equilibrium position  $\mathbf{r}_j$ . The structure factor then becomes:

$$F(\mathbf{q}) = \sum_{j=1}^{j=J} f_j(q) e^{i\mathbf{q}\cdot(\mathbf{r}_j + \Delta \mathbf{r}_j)} = \sum_{j=1}^{j=J} f_j(q) e^{i\mathbf{q}\cdot\mathbf{r}_j} e^{i\mathbf{q}\cdot\Delta\mathbf{r}_j}$$
(2.85)

If we assume a Gaussian probability density function (pdf) for each atom about its mean position, statistical methods (specifically the Baker-Hausdorff theorem) can be used to find the average value of the exponential term in equation 2.85:

$$< e^{i\mathbf{q}\cdot\Delta\mathbf{r}_j} > \approx e^{-\frac{<\left(\mathbf{q}\cdot\Delta\mathbf{r}_j\right)^2>}{2}}$$
 (2.86)

To evaluate this expression we calculate  $\mathbf{q} \cdot \Delta \mathbf{r}_j$ :

$$\mathbf{q} \cdot \Delta \mathbf{r}_{j} = |\mathbf{q}| |\Delta \mathbf{r}_{j}| \cos \phi$$

$$(\mathbf{q} \cdot \Delta \mathbf{r}_{j})^{2} = |\mathbf{q}|^{2} |\Delta \mathbf{r}_{j}|^{2} \cos^{2} \phi = \frac{16\pi^{2}}{\lambda^{2}} \sin^{2} \theta |\Delta \mathbf{r}_{j}|^{2} \cos^{2} \phi \qquad (2.87)$$

where  $\phi$  is the angle between **q** and  $\Delta \mathbf{r}_j$ . Inserting equation 2.87 into equation 2.85 and using the fact that  $\langle \cos^2 \phi \rangle = 1/3$  we can calculate the average of the exponential and find the Debye-Waller factor,  $e^{-M_j}$ :

$$< e^{i\mathbf{q}\cdot\Delta\mathbf{r}_{j}} > \approx e^{-\frac{<\left(\mathbf{q}\cdot\Delta\mathbf{r}_{j}\right)^{2}>}{2}} \approx e^{<-\frac{8\pi^{2}}{\lambda^{2}}\sin^{2}\theta|\Delta\mathbf{r}_{j}|^{2}\cos^{2}\phi>}$$
$$\approx e^{-\frac{8\pi^{2}}{\lambda^{2}}\sin^{2}\theta<|\Delta\mathbf{r}_{j}|^{2}><\cos^{2}\phi>}$$
$$\approx e^{-\frac{8\pi^{2}\sin^{2}\theta}{3\lambda^{2}}<|\Delta\mathbf{r}_{j}|^{2}>}$$
$$\approx e^{-M_{j}} \qquad (2.88)$$

This information can now be incorporated into equation 2.85 and the Debye-Waller factor absorbed into the atomic form factor to produce the modified atomic form factor  $f_j^*(q)$ :

$$F(\mathbf{q}) = \sum_{j=1}^{j=J} f_j(q) e^{-M_j} e^{i\mathbf{q}\cdot\mathbf{r}_j} = \sum_{j=1}^{j=J} f_j^*(q) e^{i\mathbf{q}\cdot\mathbf{r}_j}$$
(2.89)

#### 2.2.10 X-ray diffraction from a 3-D crystal

Consider an orthogonal 3-D unit cell defined by the lattice vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$ . The position of each atoms within the unit cell can be expressed in fractional co-ordinates  $(x_j, y_j, z_j)$ , where:

$$\mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3. \tag{2.90}$$

Neglecting the superscript to indicate the modified form factor, the structure factor for the unit cell becomes:

$$F(\mathbf{q}) = \sum_{j=1}^{j=J} f_j(q) e^{i\mathbf{q} \cdot (x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3)}.$$
 (2.91)

Now consider a 3-D crystal composed of  $N_1$ ,  $N_2$  and  $N_3$  unit cells along the three crystal axes (defined by the lattice vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$ ). The position of the origin of each unit

cell is:

$$\mathbf{R}_{n} = \mathbf{R}_{n_{1}, n_{2}, n_{3}} = n_{1}\mathbf{a}_{1} + n_{2}\mathbf{a}_{2} + n_{3}\mathbf{a}_{3}$$
(2.92)

The total scattered electric field for the 3-D crystal is:

$$\mathbf{E}_{S}(\mathbf{R}_{0}) \approx \frac{-r_{0}\mathbf{E}_{0}e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}}{|\mathbf{R}_{0}|}F(\mathbf{q})\sum_{n_{1}=0}^{N_{1}-1}\sum_{n_{2}=0}^{N_{2}-1}\sum_{n_{3}=0}^{N_{3}-1}e^{i\mathbf{q}\cdot(n_{1}\mathbf{a}_{1}+n_{2}\mathbf{a}_{2}+n_{3}\mathbf{a}_{3})}$$
$$\approx \frac{-r_{0}\mathbf{E}_{0}e^{-i|\mathbf{k}_{0}||\mathbf{R}_{0}|}}{|\mathbf{R}_{0}|}F(\mathbf{q})\sum_{n_{1}=0}^{N_{1}-1}e^{in_{1}\mathbf{q}\cdot\mathbf{a}_{1}}\sum_{n_{2}=0}^{N_{2}-1}e^{in_{2}\mathbf{q}\cdot\mathbf{a}_{2}}\sum_{n_{3}=0}^{N_{3}-1}e^{in_{3}\mathbf{q}\cdot\mathbf{a}_{3}} \qquad (2.93)$$

In a diffraction experiment the measured quantity is the intensity of the scattered wave,  $\mathbf{I}_{S}$ , which is proportional to the square modulus of the scattered electric field :

$$\mathbf{I}_{S} \propto |\mathbf{E}_{S}|^{2} \propto |F(\mathbf{q})|^{2} \left| \sum_{n_{1}=0}^{N_{1}-1} e^{in_{1}\mathbf{q}\cdot\mathbf{a}_{1}} \sum_{n_{2}=0}^{N_{2}-1} e^{in_{2}\mathbf{q}\cdot\mathbf{a}_{2}} \sum_{n_{3}=0}^{N_{3}-1} e^{in_{3}\mathbf{q}\cdot\mathbf{a}_{3}} \right|^{2}$$
(2.94)

Each of the three sums in equation 2.94 represents a geometric series which can be evaluated:

$$\left|\sum_{n_1=0}^{N_1-1} e^{in_1 \mathbf{q} \cdot \mathbf{a}_1}\right|^2 = \left|\frac{1-e^{iN_1 \mathbf{q} \cdot \mathbf{a}_1}}{1-e^{i\mathbf{q} \cdot \mathbf{a}_1}}\right|^2 = \frac{\sin^2\left(N_1 \mathbf{q} \cdot \mathbf{a}_1/2\right)}{\sin^2\left(\mathbf{q} \cdot \mathbf{a}_1/2\right)}$$
(2.95)

Primary global maxima<sup>3</sup>, with heights of  $N_1^2$ , are spaced  $2\pi$  apart in units of  $\mathbf{q} \cdot \mathbf{a}_1$ . There are  $N_1 - 2$  subsidiary local maxima, spaced  $2\pi/N_1$  apart, between the primary global maxima. For large values of  $N_1$ , the expression is sharply peaked when  $\mathbf{q} \cdot \mathbf{a}_1 = 2\pi m$ , where m is an integer and tends towards an array of delta functions, separated by a spacing of  $2\pi$ , as  $N_1 \to \infty$ . Although no analytical solution exists for the full width at half maximum (FWHM) of the global maxima, numerical calculations show that the FWHM is inversely proportional to  $N_1$  for large values of  $N_1$ .

$$\mathbf{I}_{S} \propto F(\mathbf{q})^{2} \left( \frac{\sin^{2} \left( N_{1} \mathbf{q} \cdot \mathbf{a}_{1}/2 \right)}{\sin^{2} \left( \mathbf{q} \cdot \mathbf{a}_{1}/2 \right)} \right) \left( \frac{\sin^{2} \left( N_{2} \mathbf{q} \cdot \mathbf{a}_{2}/2 \right)}{\sin^{2} \left( \mathbf{q} \cdot \mathbf{a}_{2}/2 \right)} \right) \left( \frac{\sin^{2} \left( N_{3} \mathbf{q} \cdot \mathbf{a}_{3}/2 \right)}{\sin^{2} \left( \mathbf{q} \cdot \mathbf{a}_{1}/2 \right)} \right)$$
(2.96)

<sup>3</sup>L'Hôpital's rule. If  $\frac{a(x)}{b(x)}$  is indeterminate as x approaches zero, then  $\lim_{x\to 0} \frac{a(x)}{b(x)} = \lim_{x\to 0} \frac{a'(x)}{b'(x)}$ 

## 2.2.11 The Laué conditions and derivation of the reciprocalspace lattice vectors

The diffracted intensity for the 3-D crystal will only be intense when the following conditions are met:

$$\mathbf{q} \cdot \mathbf{a_1} = 2\pi h$$
  

$$\mathbf{q} \cdot \mathbf{a_2} = 2\pi k$$
  

$$\mathbf{q} \cdot \mathbf{a_3} = 2\pi l.$$
(2.97)

These three equations are called the Laué conditions. They show that strong diffracted beams occur when the phase difference between the momentum transfer,  $\mathbf{q}$ , and all the unit cell vectors is an integer number times  $2\pi$ . This corresponds to the constructively interference of the radiation scattered by each identical layer in the crystal.

The Laué equations can then be solved to predict the conditions under which intense diffraction peaks will be observed. A geometrical interpretation of the solution to equation 2.97 can be envisaged. The vectors  $\mathbf{a}_i$  are considered to be normals to three planes  $\Pi_i$ (the distance of each plane from the origin depends upon the respective integer h, k or l) and  $\mathbf{q}$  represents the point of intersection of the three planes (see figure 2.2). Let  $\mathbf{p}_i$  be a general point which lies in the plane  $\Pi_i$ :

$$\mathbf{p_1} = \mathbf{r_1} + \lambda_1 (\mathbf{a_1} \wedge \mathbf{a_2}) + \mu_1 (\mathbf{a_3} \wedge \mathbf{a_1})$$
  

$$\mathbf{p_2} = \mathbf{r_2} + \lambda_2 (\mathbf{a_1} \wedge \mathbf{a_2}) + \mu_2 (\mathbf{a_2} \wedge \mathbf{a_3})$$
  

$$\mathbf{p_3} = \mathbf{r_3} + \lambda_3 (\mathbf{a_3} \wedge \mathbf{a_1}) + \mu_3 (\mathbf{a_2} \wedge \mathbf{a_3}),$$
(2.98)

where  $\lambda_i$  and  $\mu_i$  are allowed to be any real number to fully cover all points in the given plane. For simplicity, we choose new starting point vectors  $\mathbf{r}_i'$ , so that:

$$\lambda_1 = \lambda_2 = \alpha$$
  

$$\mu_1 = \lambda_3 = \beta$$
  

$$\mu_2 = \mu_3 = \gamma$$
(2.99)



Figure 2.2: A geometric interpretation of the Laué conditions in x-ray diffraction

At the point of intersection between the three planes  $\mathbf{q} = \mathbf{p_1} = \mathbf{p_2} = \mathbf{p_3}$ , therefore:

$$\mathbf{q} = \mathbf{r_1}' + \alpha(\mathbf{a_1} \wedge \mathbf{a_2}) + \beta(\mathbf{a_3} \wedge \mathbf{a_1})$$
  
=  $\mathbf{r_2}' + \alpha(\mathbf{a_1} \wedge \mathbf{a_2}) + \gamma(\mathbf{a_2} \wedge \mathbf{a_3})$   
=  $\mathbf{r_3}' + \beta(\mathbf{a_3} \wedge \mathbf{a_1}) + \gamma(\mathbf{a_2} \wedge \mathbf{a_3})$  (2.100)

By inspection, the only solutions are:

$$\mathbf{r_1}' = \gamma(\mathbf{a_2} \wedge \mathbf{a_3})$$
  

$$\mathbf{r_2}' = \beta(\mathbf{a_1} \wedge \mathbf{a_3})$$
  

$$\mathbf{r_3}' = \alpha(\mathbf{a_1} \wedge \mathbf{a_2}),$$
(2.101)

which means that:

$$\mathbf{q} = \alpha(\mathbf{a_1} \wedge \mathbf{a_2}) + \beta(\mathbf{a_3} \wedge \mathbf{a_1}) + \gamma(\mathbf{a_2} \wedge \mathbf{a_3})$$
(2.102)

The co-efficients  $\alpha$ ,  $\beta$  and  $\gamma$  can be determined by taking the scalar product of **q** and either **a**<sub>1</sub>, **a**<sub>2</sub> or **a**<sub>3</sub>:

$$\mathbf{q} \cdot \mathbf{a_1} = \gamma(\mathbf{a_1} \cdot \mathbf{a_2} \wedge \mathbf{a_3}) \tag{2.103}$$

Comparison with equation 2.97 shows that:

$$\gamma = \frac{2\pi h}{\mathbf{a_1} \cdot \mathbf{a_2} \wedge \mathbf{a_3}}.\tag{2.104}$$

Similar expressions for  $\alpha$  and  $\beta$  can be inserted, along with  $\gamma$ , into equation 2.102:

$$\mathbf{q} = \frac{2\pi h(\mathbf{a_2} \wedge \mathbf{a_3})}{\mathbf{a_1} \cdot \mathbf{a_2} \wedge \mathbf{a_3}} + \frac{2\pi k(\mathbf{a_3} \wedge \mathbf{a_1})}{\mathbf{a_1} \cdot \mathbf{a_2} \wedge \mathbf{a_3}} + \frac{2\pi l(\mathbf{a_1} \wedge \mathbf{a_2})}{\mathbf{a_1} \cdot \mathbf{a_2} \wedge \mathbf{a_3}} = h\mathbf{b_1} + k\mathbf{b_2} + l\mathbf{b_3}$$
(2.105)

where:

$$\mathbf{b_1} = \frac{2\pi(\mathbf{a_2} \wedge \mathbf{a_3})}{\mathbf{a_1} \cdot \mathbf{a_2} \wedge \mathbf{a_3}}$$

$$\mathbf{b_2} = \frac{2\pi(\mathbf{a_3} \wedge \mathbf{a_1})}{\mathbf{a_1} \cdot \mathbf{a_2} \wedge \mathbf{a_3}}$$

$$\mathbf{b_3} = \frac{2\pi(\mathbf{a_1} \wedge \mathbf{a_2})}{\mathbf{a_1} \cdot \mathbf{a_2} \wedge \mathbf{a_3}}$$
(2.106)

The vectors  $\mathbf{b}_i$  are called the reciprocal lattice vectors. Note that:

$$\mathbf{a}_{\mathbf{i}} \cdot \mathbf{b}_{\mathbf{j}} = 2\pi \delta_{i,j} \tag{2.107}$$
If i = j then  $\delta_{i,j} = 1$ , or if  $i \neq j$  then  $\delta_{i,j} = 0$ . The intensity of the diffracted x-ray beam is negligible except when the momentum transfer vector, **q**, corresponds to a reciprocal lattice point (labelled by the integers h, k and l). Equation 2.94 shows that the relative diffracted intensity at a particular reciprocal lattice point depends upon the magnitude of structure factor:

$$I_{h,k,l} \propto F_{h,k,l}^2 \tag{2.108}$$

In a diffraction experiment, measurement of the relative strengths of the diffraction peaks allows the calculation of the structure factor for the crystal.

#### 2.2.12 Semi-kinematical surface diffraction

We now consider diffraction not from an infinite 3-D crystal, but from a semi-infinite crystal [10]. This structure will consist of two parts: the bulk crystal terminated in the  $\mathbf{a}_3$  direction; and a layer or layers of atoms at the surface of the crystal, whose relative positions are different from atoms in the bulk (atoms at the surface of the crystal, with unsatisfied chemical bonds, "reconstruct" (in the plane of the truncation) and "relax" (perpendicular to the plane of truncation) to minimise their energy). Since the scattered waves from the bulk and the surface regions are coherent, the total field is simply the sum of the scattered electromagnetic waves from the bulk and the surface:

$$\mathbf{E}_{total}(\mathbf{q}) = \mathbf{E}_{bulk}(\mathbf{q}) + \mathbf{E}_{surface}(\mathbf{q})$$
(2.109)

The dynamical treatment of the bulk scattering (including absorption) and the kinematical treatment of the scattering from the surface layers is referred to as the semi-kinematical treatment for the total structure.

#### The truncated bulk contribution

Consider a sample with a bulk unit cell defined by the orthogonal lattice vectors  $\mathbf{A}_i$ (throughout this work, capital letters and lower case letters are assigned to denote bulk and surface lattice vectors respectively). For a truncated sample we can consider  $N_1$  and  $N_2$  bulk unit cells in the  $\mathbf{A}_1$  and  $\mathbf{A}_2$  directions. In the  $\mathbf{A}_3$  direction we consider the sample to be truncated at  $N_3 = 0$  and to extend to infinity in a direction anti-parallel to  $\mathbf{A}_3$ . An attenuation factor  $\mu$  is also included to model the absorption of the x-ray beam perpendicular to the surface. The structure factor for the truncated bulk is:

$$\mathbf{E}_{bulk}(\mathbf{q}) \propto F(\mathbf{q}) \sum_{n_1=0}^{N_1-1} e^{in_1\mathbf{q}\cdot\mathbf{A}_1} \sum_{n_2=0}^{N_2-1} e^{in_2\mathbf{q}\cdot\mathbf{A}_2} \sum_{n_3=0}^{-\infty} e^{(i\mathbf{q}\cdot\mathbf{A}_3+\mu)n_3}$$
$$\propto F(\mathbf{q}) \sum_{n_1=0}^{N_1-1} e^{in_1\mathbf{q}\cdot\mathbf{A}_1} \sum_{n_2=0}^{N_2-1} e^{in_2\mathbf{q}\cdot\mathbf{A}_2} \left(\frac{1}{1-e^{-i\mathbf{q}\cdot\mathbf{A}_3-\mu}}\right)$$
(2.110)

Equation 2.110 gives the location in reciprocal space of the crystal truncation rods (CTRs), and also the intensity of the CTRs in the  $A_3$  direction (perpendicular to the plane of truncation).

#### The surface contribution

We now consider an extra layer (or layers) of atoms at a distance d (the layer is "relaxed" from it's bulk position) above the truncated sample surface. Due to reconstruction (symmetry breaking caused by atoms moving from their bulk in-plane positions), the unit cell describing the surface structure is often larger than the bulk unit cell. Figure 2.3 shows a surface unit cell in which  $\mathbf{a}_1 = 2\mathbf{A}_1$ ,  $\mathbf{a}_2 = 3\mathbf{A}_2$  and  $\mathbf{a}_3 = \mathbf{A}_3$ . The structure factor for a surface comprising  $P_1$  unit cells in the  $\mathbf{a}_1$  direction,  $P_2$  unit cells in the  $\mathbf{a}_2$  direction and a single unit cell in the  $\mathbf{a}_3$  direction ( $\mathbf{a}_3$  is conventionally chosen to lie perpendicular to the plane containing  $\mathbf{a}_1$  and  $\mathbf{a}_2$ ) is:

$$\mathbf{E}_{surface}(\mathbf{q}) \propto F(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{d}} \sum_{p_1=0}^{P_1-1} e^{ip_1\mathbf{q}\cdot\mathbf{a}_1} \sum_{p_2=0}^{P_2-1} e^{ip_2\mathbf{q}\cdot\mathbf{a}_2}$$
$$\propto F(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{d}} \sum_{p_1=0}^{P_1-1} e^{ip_1\mathbf{q}\cdot\mathbf{2A}_1} \sum_{p_2=0}^{P_2-1} e^{ip_2\mathbf{q}\cdot\mathbf{3A}_2}$$
(2.111)

which is totally independent of the momentum transfer perpendicular to the surface  $\mathbf{q} \cdot \mathbf{a}_3$ (the third Laue condition has been eliminated). A phase term  $(e^{i\mathbf{q}\cdot\mathbf{d}})$  has been included



Figure 2.3: The surface (red) unit cell "relaxed" to a distance d above the bulk unit cells (green). Reconstruction of the surface atoms produces a surface unit cell that is larger than the bulk unit cell

in equation 2.111 to allow the addition of the bulk and surface contributions to the total scattering. Intense diffraction peaks are observed at the lines of intersection between the set of planes which are perpendicular to  $\mathbf{a}_1$  and  $\mathbf{a}_2$  (and parallel to  $\mathbf{a}_3$ ). Each line of intersection, or "rod", is sharp in the  $\mathbf{a}_1$  and  $\mathbf{a}_2$  directions, but continuous in the  $\mathbf{a}_3$  direction.

The surface reciprocal vectors for this system can be calculated using equation 2.106 and are shown in figure 2.4:

$$\mathbf{b}_{1} = \frac{2\pi(\mathbf{a}_{2} \wedge \mathbf{a}_{3})}{\mathbf{a}_{1} \cdot \mathbf{a}_{2} \wedge \mathbf{a}_{3}} = \frac{2\pi(3\mathbf{A}_{2} \wedge \mathbf{A}_{3})}{2\mathbf{A}_{1} \cdot 3\mathbf{A}_{2} \wedge \mathbf{A}_{3}} = \frac{\mathbf{B}_{1}}{2}$$
$$\mathbf{b}_{2} = \frac{2\pi(\mathbf{a}_{3} \wedge \mathbf{a}_{1})}{\mathbf{a}_{1} \cdot \mathbf{a}_{2} \wedge \mathbf{a}_{3}} = \frac{2\pi(\mathbf{A}_{3} \wedge 2\mathbf{A}_{1})}{2\mathbf{A}_{1} \cdot 3\mathbf{A}_{2} \wedge \mathbf{A}_{3}} = \frac{\mathbf{B}_{2}}{3}$$
(2.112)

Reconstruction of the surface layers leads to a reduced symmetry of the surface unit cell (in comparison to the smaller, bulk unit cell) and produces "surface rods" in the space between the CTRs. The reciprocal lattice from a "real" crystal structure is an amalgamation of the CTRs from the truncated crystal and the surface rods from the



**Figure 2.4:** A reciprocal-space diagram showing: the crystal truncation rods (CTRs) produced the truncation of the sample; and surface rods produced by reconstruction of the surface layers leading to the reduced symmetry of the surface unit cell

surface cell. The location, in the plane of the surface, of all the atoms in the real space surface unit cell determines the relative strengths of the rods. In SXRD experiments, one type of measurement is to scan through reciprocal space with  $\mathbf{B}_3$  approximately equal to zero (in-plane measurements) to determine the location and relative strength of each rod. The strength of each rod is determined by the location in the plane of the surface, of all the atoms in the real space surface unit cell. Another type of measurement is to scan along the CTRs in the direction of  $\mathbf{B}_3$  (out-of-plane). These scans give information about the structure of the sample perpendicular to the sample surface.

The symmetry of the location of the diffraction peaks is used to construct a trial model for the surface. Unfortunately, a wide range of possible structures have the same symmetry predicted by the diffraction peaks. Chemical principles (such as the fact that bonding between certain chemical elements is preferable) and established models from similar systems are used to select the most likely structure. From this trial model the diffracted intensities are calculated and compared with the experimental value. An iterative procedure is then used to modify the trial structure until the calculated diffraction intensities match the experimental values.

## 2.3 Auger electron spectroscopy

Auger Electron spectroscopy (AES) is used predominately to analyse the cleanliness and chemical composition of a surface which has been freshly prepared under UHV conditions. The major interaction mechanism between free electrons and the solid through which they are travelling is the excitation of plasmon waves, whose energy is determined solely by the electron density in the solid. The number density of electrons in the valence band is approximately constant for all materials. Consequently, there exists a quasi-universal dependence of the mean free path of electrons in solids as a function of their energy. Electrons with kinetic energies of between 10 and 1000 eV have a mean free path in a solid of less than 10Å.

#### Theory of AES

A high energy electron beam (1-2 keV) is directed at the sample. The backscattered electrons are collected and their energy spectrum, N(E), analysed. An incident electron scatters off a bound, core level electron, producing an ionised core level (Figure 2.6, part A). The incident electron and the scattered core electron (both of which now have ill-defined energies due to the complexity of the scattering process) both leave the atom. The hole left in the core level is quickly filled by an electron from a higher energy shell (Figure 2.6, part B). This transition energy is absorbed by a different electron, the so called *Auger* electron, which can then escape from its bound state. The kinetic energy of the Auger electron can be found from the conservation of energy:

$$K.E_{\text{Auger}} = E_{2p} + E_{2s} - E_{1s} \tag{2.113}$$

where  $E_{2p}$ ,  $E_{2s}$  and  $E_{1s}$  represent the binding energies of the 2p, 2s and 1s core levels respectively (N. B. The binding energies are all negative). Since  $E_{2s} - E_{1s} > |E_{2p}|$ the kinetic energy will be positive. It is also important to note that the Auger electron's energy depends only upon the atomic binding energies, and not upon the incident electron beam energy.

Most electrons lose arbitrary amounts of energy through multiple, inelastic collisions, those which escape from the sample produce a continuous energy spectrum. The primary, Auger electrons have an element dependent set of energies and produce small peaks on the continuous energy spectrum (see figure 2.5). Measurement of the emitted Auger electron kinetic energies (which will be related to the energy differences between core levels) can be used to identify the type of atom from which the Auger electron originated. This technique is surface sensitive because only Auger electrons that are emitted within approximately 10 Å of the sample surface can escape without encountering further scattering.



Figure 2.5: Energy spectrum of detected electrons, showing the continuous background produced by secondary, multiply scattered electrons, and a series of characteristic peaks produced by primary Auger electrons



Figure 2.6: The Auger process, an incident electron is scattered off a core level electron, producing an ionised core level (left). The core level hole is filled by an electron from a higher energy shell, this energy is absorbed by the Auger electron which then escapes from its bound state (right)

#### **Experimental** apparatus

Figure 2.7 shows a schematic diagram of a retarding field analyser (RFA) used for AES. An electron gun projects through the fluorescent collector screen and produces a stream of electrons, with typical energies of 2 keV which strikes the sample at approximately normal incidence. The inner and outer grids are earthed to maintain a uniform electromagnetic





field near the sample and to shield the collector. The middle two grids are connected together and floated to a negative voltage V. This voltage is composed of a negative retarding potential  $V_{\text{retard}}$  (just less than the energy of the incident electron beam) and a

sinusoidal modulating voltage (produced by an oscillator, typically 2–5 V):

$$V = V(V_{\text{retard}}, V_0, \omega, t) = V_{\text{retard}} + V_0 \sin \omega t.$$
(2.114)

where  $V_0$  and  $\omega$  are the amplitude and frequency of the modulated voltage respectively. The current, I, obtained from the collector will be a function of the grid voltage, V, and hence a function of the constant retarding grid potential and the modulating voltage:

$$I = I(V) = I(V_{\text{retard}} + V_0 \sin \omega t)$$
(2.115)

The expression for the collected current I(V), can be expanded, in a Taylor series, about the point  $V = V_{\text{retard}}$ :

$$I(V_{\text{retard}} + V_0 \sin \omega t) = I(V_{\text{retard}}) + \frac{V_0}{1!} \sin \omega t \frac{dI}{dV} + \frac{V_0^2}{2!} \sin^2 \omega t \frac{d^2I}{dV^2} + \dots$$
(2.116)

where the differentials of I with respect to V, are all evaluated at  $V = V_{\text{retard}}$ . The higher powers of the function sine can be expressed in terms of sine and cosine functions:

$$\sin^{2} x = \frac{1}{2} - \frac{\cos 2x}{2}$$
  

$$\sin^{3} x = \frac{3\sin x}{4} - \frac{\sin 3x}{4}$$
  

$$\sin^{4} x = \frac{3}{8} - \frac{\cos 2x}{2} + \frac{\cos 4x}{8}$$
(2.117)

These expressions can then be inserted into equation 2.116 and terms containing similar multiples of  $\omega$  grouped together:

$$I(V_{\text{retard}}, V_0, \omega, t) = \begin{pmatrix} \frac{V_0^2}{4} \frac{d^2 I}{dV^2} + \frac{V_0^4}{64} \frac{d^4 I}{dV^4} + \dots \end{pmatrix}$$
  
+  $\begin{pmatrix} V_0 \frac{dI}{dV} + \frac{V_0^3}{8} \frac{d^3 I}{dV^3} + \dots \end{pmatrix} \sin \omega t$   
+  $\begin{pmatrix} -\frac{V_0^2}{4} \frac{d^2 I}{dV^2} - \frac{V_0^4}{48} \frac{d^4 I}{dV^4} + \dots \end{pmatrix} \cos 2\omega t$ 

$$+ \dots$$
 (2.118)

Since the energy distribution and the differential of the energy distribution are proportional to:

$$N(E) \propto \frac{dI}{dV}$$
 and  $\frac{dN(E)}{dV} \propto \frac{d^2I}{dV^2}$ , (2.119)

analysis of equation 2.118 shows that:

- the component of the collected current that has a frequency of  $\omega$  is, to a first approximation, proportional to  $\frac{dI}{dV}$  (neglecting higher order terms);
- and the component of the collected current that has a frequency of  $2\omega$  is, to a first approximation, proportional to  $\frac{d^2I}{dV^2}$  (neglecting higher order terms)

## 2.4 Co-ordinate transformations

## 2.4.1 General transformations

Co-ordinate transformations are frequently employed in crystallography. Examples include: transformations between bulk and surface co-ordinates; and from the real-space lattice to the reciprocal-space lattice. In most texts, only transformations between orthogonal basis sets are considered (i.e the axes are mutually perpendicular). However, in many cases, the surface unit vectors are non-orthogonal; this motivates the derivation of the more general transformation of co-ordinates between any two frames of reference. Let **r** represent the vector displacement of a point P, from the origin O, which can be expressed in terms of two basis sets  $\mathbf{a}_i$  and  $\mathbf{b}_i$ :

$$\overrightarrow{OP} = \mathbf{r} = p_1 \mathbf{a}_1 + p_2 \mathbf{a}_2 + p_3 \mathbf{a}_3 = q_1 \mathbf{b}_1 + q_2 \mathbf{b}_2 + q_3 \mathbf{b}_3$$
 (2.120)

Our goal is to determine the transformation which converts between the two frames of reference. A scalar version of the vector equation 2.120 can be obtained by taking the scalar product of equation 2.120 and  $\mathbf{a}_2 \wedge \mathbf{a}_3$ .

$$\mathbf{r} \cdot (\mathbf{a}_2 \wedge \mathbf{a}_3) = p_1 \mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3 + p_2 \mathbf{a}_2 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3 + p_3 \mathbf{a}_3 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3 \qquad (2.121)$$

$$= q_1 \mathbf{b}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3 + q_2 \mathbf{b}_2 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3 + q_3 \mathbf{b}_3 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3 \qquad (2.122)$$

The nature of the vector product dictates that  $p_2\mathbf{a}_2 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3 = p_3\mathbf{a}_3 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3 = 0$ . Rearrangement leads to an expression for,  $p_1$ , in terms of the alternate frame of reference:

$$p_1 = \sum_{n=1}^{3} q_n \frac{\mathbf{b}_n \cdot \mathbf{a}_2 \wedge \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3}$$
(2.123)

The second and third components of the position in the new frame of reference can be obtained in a similar manner with a suitable choice of vector to "dot" with  $\mathbf{r}$ .

$$p_2 = \sum_{n=1}^{3} q_n \frac{\mathbf{b}_n \cdot \mathbf{a}_3 \wedge \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} \quad \text{and} \quad p_3 = \sum_{n=1}^{3} q_n \frac{\mathbf{b}_n \cdot \mathbf{a}_1 \wedge \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} \tag{2.124}$$

This information can be assimilated to form a matrix equation:

$$\begin{bmatrix} p_1 \\ p_2 \\ p_3 \end{bmatrix} = \begin{bmatrix} \frac{\mathbf{b}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} & \frac{\mathbf{b}_2 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} & \frac{\mathbf{b}_3 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} \\ \frac{\mathbf{b}_1 \cdot \mathbf{a}_3 \wedge \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} & \frac{\mathbf{b}_2 \cdot \mathbf{a}_3 \wedge \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} & \frac{\mathbf{b}_3 \cdot \mathbf{a}_3 \wedge \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} \\ \frac{\mathbf{b}_1 \cdot \mathbf{a}_1 \wedge \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} & \frac{\mathbf{b}_2 \cdot \mathbf{a}_1 \wedge \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} & \frac{\mathbf{b}_3 \cdot \mathbf{a}_1 \wedge \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix}$$
(2.125)

#### 2.4.2 Orthogonal transformations

The simpler orthogonal transformations will now be derived as a special case of the general transformation in equation 2.125. Let the vectors within each of the two basis sets ( $\mathbf{a}_i$  and  $\mathbf{b}_i$ ) be mutually perpendicular (i.e form right handed sets) and have unit length.

$$\mathbf{a}_{1} \cdot \mathbf{a}_{2} \wedge \mathbf{a}_{3} = 1 \qquad \mathbf{b}_{1} \cdot \mathbf{b}_{2} \wedge \mathbf{b}_{3} = 1$$
$$\mathbf{a}_{1} \wedge \mathbf{a}_{2} = \mathbf{a}_{3} \qquad \mathbf{b}_{1} \wedge \mathbf{b}_{2} = \mathbf{b}_{3}$$
$$\mathbf{a}_{2} \wedge \mathbf{a}_{3} = \mathbf{a}_{1} \qquad \mathbf{b}_{2} \wedge \mathbf{b}_{3} = \mathbf{b}_{1}$$
$$\mathbf{a}_{3} \wedge \mathbf{a}_{1} = \mathbf{a}_{2} \qquad \mathbf{b}_{3} \wedge \mathbf{b}_{1} = \mathbf{b}_{2}$$
$$(2.126)$$

These equations can then be substituted into equation 2.125.

$$\begin{bmatrix} p_1 \\ p_2 \\ p_3 \end{bmatrix} = \begin{bmatrix} \mathbf{b}_1 \cdot \mathbf{a}_1 & \mathbf{b}_2 \cdot \mathbf{a}_1 & \mathbf{b}_3 \cdot \mathbf{a}_1 \\ \mathbf{b}_1 \cdot \mathbf{a}_2 & \mathbf{b}_2 \cdot \mathbf{a}_2 & \mathbf{b}_3 \cdot \mathbf{a}_2 \\ \mathbf{b}_1 \cdot \mathbf{a}_3 & \mathbf{b}_2 \cdot \mathbf{a}_3 & \mathbf{b}_3 \cdot \mathbf{a}_3 \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix}$$
(2.127)

Since  $\mathbf{b}_i \cdot \mathbf{a}_j = |\mathbf{b}_i| |\mathbf{a}_j| \cos \theta_{ij}$  (where  $\theta_{ij}$  is the angle between the basis vectors  $\mathbf{b}_i$  and  $\mathbf{a}_j$ )

and  $|\mathbf{b}_i| = |\mathbf{a}_j| = 1$ , equation 2.127 can be simplified.

$$\begin{bmatrix} p_1 & p_2 & p_3 \end{bmatrix} = \begin{bmatrix} q_1 & q_2 & q_3 \end{bmatrix} \begin{bmatrix} \cos \theta_{11} & \cos \theta_{21} & \cos \theta_{31} \\ \cos \theta_{12} & \cos \theta_{22} & \cos \theta_{32} \\ \cos \theta_{13} & \cos \theta_{23} & \cos \theta_{33} \end{bmatrix}$$
(2.128)

## Chapter 3

## **Experimental considerations**

## 3.1 Introduction

In this chapter we describe the experimental techniques and apparatus used to prepare and characterise atomically clean, well ordered III-V semiconductor surfaces using synchrotron surface x-ray diffraction (SXRD) and Auger electron spectroscopy (AES). Ultra high vacuum (UHV) conditions are required for most surface science experiments, we explain how UHV is achieved, maintained and monitored throughout. III-V semiconductor samples are cleaved from 3 inch diameter, circular wafers and attached to molybdenum backing plates and sample holders, before been loaded into Leicester University's xray chamber (LUXC). Brief descriptions of LUXC and the available surface science preparation and analysis tools are given. X-rays interact very weakly with matter. To obtain appreciable surface x-ray scattering, an intense source of x-rays from a 2nd or 3rd generation synchrotron source is required. An overview of the production of synchrotron radiation is given. We describe how LUXC is coupled to the 6-circle diffractometer at station 9.4 at the synchrotron radiation source (SRS), Daresbury and how x-ray diffraction measurements are made. To compare the detected integrated x-ray intensities, a number of correction factors need to be applied to the experimental data. This allows direct comparison with the theoretical scattering discussed in section 2.2.

## **3.2** The need for ultra high vacuum

Vacuum conditions are essential for most surface science experiments for the following reasons:

- to maintain a contaminant free environment during the experiment;
- and to allow the sample surface to be studied using electronic, photonic and ionbased probes without undue interactions with residual gas molecules.

The three main units of pressure used in vacuum technology are the millibar (mbar), the Pascal (Pa), and the Torricelli (Torr):

For surface spectroscopy, the mean free path of the probe and detected particles must be significantly greater than the dimensions of the measuring apparatus. This ensures negligible interactions between the incident and detected particles and the residual gas molecules. The mean free path of a neutral particle,  $\lambda$ , calculated using a simple hard sphere collision model is:

$$\lambda[m] = \frac{kT}{\sqrt{2}P\sigma},\tag{3.2}$$

where k is Boltzmann's constant  $(1.38 \times 10^{-23} \text{ J K}^{-1})$ , T is the temperature [K], P is the pressure [N m<sup>-2</sup>] and  $\sigma$  is the molecular cross section [m<sup>2</sup>] which is equal to  $\pi d^2$ , where d is the molecular diameter. Assuming room temperature conditions (T = 273 K) and a molecular diameter of the order of 2Å, table 3.1 shows the calculated mean free path as a function of pressure.

The next step is to calculate how long a prepared surface remains contaminant free. Derived using the ideal gas laws and Maxwell-Boltzmann statistics, the Hertz-Knudsen formula can be used to calculate the incident flux of residual gas molecules per unit time per unit area at the sample surface:

$$F = \frac{P}{\sqrt{2\pi m k T}},\tag{3.3}$$

where m is the average molecular mass of residual gas molecules. The conventional unit of dose (adsorbate coverage) is the Langmuir which is defined to be equal to  $10^{-6}$  Torr s. Assuming a monolayer coverage of the order of  $10^{19}$  molecules per m<sup>2</sup> and a sticking coefficient of 1 (all incident molecules bond to the sample surface on impact) table 3.1 shows the time required to contaminate the surface with a monolayer of adsorbates, as a function of the residual gas pressure. Table 3.1 shows that a medium vacuum pressure of  $< 10^{-5}$ mbar is sufficient for a negligible interaction between the incident and detected molecular probes and the residual gas molecules. However, table 3.1 shows that an ultra high

Pressure regime	Pressure	Mean free path, $\lambda$	Contamination time
Atmospheric	100 mbar	$1 \times 10^{-7} \mathrm{m}$	$10^{-9} { m s}$
Low vacuum (LV)	1 mbar	$1 \times 10^{-4} \mathrm{m}$	$10^{-6} { m s}$
Medium vacuum (MV)	$10^{-3}$ mbar	$1 \times 10^{-1} \text{ m}$	$10^{-3} { m s}$
High vacuum (HV)	$10^{-6}$ mbar	$1 \times 10^2 \text{ m}$	1 s
Ultra high vacuum (UHV)	$10^{-10}$ mbar	$1 \times 10^{6} \text{ m}$	10 <sup>4</sup> s

**Table 3.1:** The calculated molecular mean free path and the time required for one monolayer of contamination to build up on the sample surface, as a function of gas pressure at room temperature

vacuum of less than  $< 10^{-10}$  mbar is required to maintain an atomically clean prepared surface throughout the duration of a surface science experiment.

## 3.3 Sample manufacture

Under clean conditions in a laminar air flow cabinet, 8 mm  $\times$  8mm sections are cleaved from circular, three inch III-V semiconductor wafers. The wafers are preferentially cleaved along a crystallographic axis by touching the point of a clean (sterilised) scalpel blade to the edge of the wafer and applying a small amount of pressure. Dry, research grade nitrogen or helium gas is blown over the sample surface to gently remove any small segments of wafer liberated during the cleavage process. 10mm  $\times$  8mm  $\times$  1mm ultra-sonically cleaned molybdenum backing plates are outgassed at 700°C under UHV conditions, before being scored, using a scalpel blade, to increase adhesion. A small nugget (approx 1mm in diameter) of indium is placed at the centre of the molybdenum backing plate which is then slowly heated and stabilised at the melting point of indium (178°C). The cleaved wafer sections are then gently bonded to the molybdenum backing plate using the molten indium as a seal (shown on the left in figure 3.1). After cooling, the samples are mounted on an x-ray diffraction sample holder, using two thin tantalum clips which tightly grip the exposed end sections of the molybdenum backing plate (shown on the right in figure 3.1).



Figure 3.1: An  $8 \times 8$  mm cleaved wafer section bonded to an  $8 \times 10$  mm molybdenum back plate using a small amount of indium seal (left), and the x-ray diffraction sample holder showing the tantalum clips used to grip the exposed sections of the molybdenum backing plate (right)

## 3.4 The LUXC characterisation chamber

### 3.4.1 Pumping and pressure measurement

Evacuating the LUXC characterisation chamber is carried out using a range of pumps:

- Carbon vane pump: atmospheric pressure  $\rightarrow 150$  mbar
- Sorption pump: 150 mbar  $\rightarrow 10^{-4}$  mbar
- Diffusion pump (backed by a rotary pump):  $10^{-4}$  mbar  $\rightarrow 10^{-8}$  mbar
- Varian 400 litres s<sup>-1</sup> ion pump:  $10^{-4} \rightarrow 10^{-10}$  mbar

- Liquid nitrogen cooled, titanium sublimation pump:  $10^{-9} \rightarrow 10^{-11}$  mbar
- Turbo-molecular pump: atmospheric pressure  $\rightarrow 10^{-10}$  mbar

A range of sensors, encompassing the entire range of pressures from atmospheric pressure down to UHV, are used to measure the pressure at a number of points within LUXC:

- Ion gauge:  $10^{-5}$  mbar  $\rightarrow 10^{-11}$  mbar
- Pirani gauge: Atmospheric pressure  $\rightarrow 10^{-11}$  mbar
- Penning gauge:  $10^{-3}$  mbar  $\rightarrow 10^{-8}$  mbar

A base pressures of  $5 \times 10^{-11}$  mbar is routinely achieved after "baking-out" LUXC for 24 hours at 150°C to liberate water vapour bonded to the inside of the chamber.

#### 3.4.2 Sample preparation and analysis equipment

LUXC (see figure 3.2) is equipped with the following surface science sample preparation and analysis tools:

- A Vacuum Generators (VG) SX200 residual gas mass spectrometer. Used to characterise the relative concentrations of the residual gases present within the SXRD chamber, allowing real time analysis of the UHV conditions. This is particularly useful to locate leaks before the bake-out procedure and to measure the purity of the Ar gas used during sputtering
- Either rear-view LEED to monitor the atomic order of the sample surface, or a loadlock sample transfer system, differentially pumped by a portable turbo-molecular pump
- A 0-10keV Ar<sup>+</sup> ion gun, used to sputter surface impurities

- Ports are available to house up to six Knudsen cell evaporators
- A VG LEG31 electron gun and a VSW HA50 hemispherical electron analyser used to carry out Auger electron spectroscopy (AES)
- A cylindrical section beryllium window through which the incident and diffracted x-ray beams can enter the chamber (200° (vertical) by 30° (horizontal) angular access)
- An infrared pyrometer to remotely measure the sample temperature

#### 3.4.3 The rotary seal

Samples mounted on sample holders are connected, via a collet mechanism and a 4-pin arrangement, to the rotary seal arm in LUXC either before evacuating the entire chamber, or after UHV is attained via the optional load-lock, sample transfer system. Electrical contact with the sample and sample holder is made via the 4-pin system. Two pins are connected to a thoriated tungsten filament housed within the sample holder, allowing radiative heating of the molybdenum backing plate. The two remaining pins make contact with the sample backing plate, and are used for either high voltage electron bombardment heating or voltage modulation of the sample during AES. A chromel-alumel thermocouple, contained within the rotary seal, can be attached to one of the molybdenum screws which holds the tantalum plate to the molybdenum backing plate, allowing thermal contact with the sample. The thermocouple is used, in conjunction with the observed melting point of indium, to calibrate the remote infrared pyrometer. The entire rotary seal mechanism is differentially pumped: the low vacuum section of the rotary seal is pumped to  $10^{-3}$ mbar using a rotary pump; the high vacuum section is pumped to  $10^{-6}$  mbar using a 50 litres  $s^{-1}$  Balzer turbo-molecular pump. Flexible bellows built into the rotary seal mean that the sample can be rotated through a full 360° and angled at up to  $\pm 15^{\circ}$ , relative to LUXC, during x-ray measurements without detectable leakage from the high vacuum rotary seal section to the main UHV chamber even at base pressures of  $10^{-10}$  mbar.



Figure 3.2: The surface x-ray diffraction (SXRD) chamber

## **3.5** Synchrotron radiation

In 1912 W. D. Coolidge developed a vacuum tube in which electrons emitted by a glowing filament were accelerated towards a water cooled metal anode, the impact producing a continuous *bremsstrahlung* x-ray spectrum and a sharp line spectrum of, material dependent, fluorescent x-rays. The limiting factor in the x-ray intensity is set by how efficiently heat can be removed from the anode. Spinning the anode allowed extra heat to be dissipated, increasing the power output. It wasn't until the 1960's that rotating anode sources became commercially available.

In the 1970's it was realised that synchrotron radiation emitted by charged particles accelerated around storage rings, for use in high energy nuclear physics experiments, could provide a significantly more intense source of x-rays, the so called 1st generation synchrotron sources. Dedicated 2nd and 3rd generation sources can now produce synchrotron radiation of the order of  $10^{12}$  times brighter than early lab-based x-ray sources. New 3rd generation synchrotron sources are currently being planned and built, including Diamond at Oxford, which will be operational by 2007. The invention of the free-electron laser also looks likely to revolutionise the production of x-rays (4th generation source).

In an dedicated electron synchrotron, a stream of electrons is produced by an electron gun. The electrons are accelerated in two stages: a primary stage where approximately 10<sup>10</sup> electrons are bunched together and accelerated to approximately half the speed of light by a linear accelerator (linac) using oscillating electromagnetic fields produced by radio frequency (RF) cavities; and a secondary acceleration stage where the electron bunches are accelerated up to almost the speed of light in a circular booster synchrotron. The high energy (600 MeV) electrons are then "injected" into an evacuated storage ring composed of straight sections linked together to form a continuous loop. Once a sufficient storage current is achieved, the electron energy is increased to 2 GeV.

Dipole bending magnets curve the electron beam around the junctions to the straight

sections of the storage ring using the Lorentz force. Focusing quadrupole magnets contained within the straight sections of the storage ring are used to collimate the electron beam. At any one time, the storage ring at the SRS, Daresbury, can contain up to 160 electron bunches, each bunch of 50–100 ps duration, separated from the adjacent bunches by 2 ns. Each bunch loses energy during each circuit of the storage ring. To ensure stability of the electron orbit, each bunch periodically receives an energy energy boost from an RF cavity. The electron beam is typically refilled once per day to counteract the gradual depletion of the beam current due to electron collisions with residual gas molecules contained within the evacuated storage ring. A circulating current of > 250 mA and lifetimes of > 24 hours are routinely achieved at the SRS.

Electrons accelerated around the storage ring at relativistic speeds produce a highly collimated flattened cone of concentrated radiation in the direction of the electrons velocity, tangential to the storage ring. The flux and brightness of the radiation produced by the dipole bending magnets is increased many thousands of times by the use of insertion devices located on the straight sections of the storage ring. Insertion devices consist of two rows of small magnets with alternating polarity. They induce a sinusoidal motion to the electron beam in the horizontal plane, causing radiation to be emitted and delivered to purpose built beamline stations. There are two main types of insertion device:

- multipole wigglers: a flattened cone of radiation is produced at each "wiggle" of the electron beam caused by SC magnets. The overall intensity of the emitted radiation is enhanced by a factor of 2 N, where N is the number of periods. The intensity from each "wiggle" adds to give the total intensity. The x-ray spectrum is the same as that of a bending magnet with an identical magnetic field strength.
- undulators: permanent magnets are used to produce electron oscillations with smaller amplitudes. This is specially designed so that radiation emitted by a given electron at one oscillation is in phase with the radiation from the following oscillation. Constructive interference occurs, producing a narrower cone of quasi-monochromatic radiation, up to 10,000 times more intense than a wiggler.

The SRS contains a total of 5 insertion devices: two x-ray (high field 5T superconducting) wigglers; a VUV SXR undulator; and two multipole wigglers delivering x-ray and VUV radiation to approximately 30 beamline station. For an undulator the radiation from each oscillation of an electron is coherent, leading to constructive interference and an increase in the intensity of emitted radiation. However, the lack of spatial coherence in the electron beam means that radiation produced by an individual electron isn't in phase with the radiation produced by all the other electrons. In a free electron laser (4th generation source) the electrons in a bunch are ordered spatially to match the wavelength of the emitted radiation so that all the radiation produced is coherent. This leads to a massive increase in the brilliance of the beam (100 to  $10^5$  times more brilliant than an undulator source).



Figure 3.3: A schematic of the synchrotron and storage ring (left), and a schematic of an undulator showing the sinusoidal motion imparted to the electron beam by alternating polarity magnets (right)

## **3.6** Station 9.4 at the SRS, Daresbury

Radiation from the 5 tesla wiggler is focused by a toroidal silicon mirror coated with 500 Å of platinum, and monochromated by a water cooled, channel cut silicon(111) crystal. Monochromatic radiation (with a tunable wavelength of between 0.7 and 2.5 Å) reaches a focus at the centre of the quasi-6-circle diffractometer at station 9.4. The full width at half maximum (FWHM) of the beam profile at the sample position is typically 0.6 mm (vertically) and 2.4 mm (horizontally). Pre-sample slits typically define the x-ray beam to be of size  $1 \times 0.6$  mm. Aluminium and lead films of varying thickness can optionally be mechanically inserted into the direct x-ray beam for attenuation purposes. A gas filled ion chamber, located downstream from the attenuation filters, is used to monitor the intensity of the incident x-ray beam at the sample. This allows the normalisation of temporal fluctuations in the beam intensity. Diffracted beams are detected by a liquid nitrogen cooled, solid state, germanium detector mounted on the diffractometer.

Figure 3.4 shows the LUXC coupled to the quasi-6-circle diffractometer at station 9.4. The incident and scattered x-ray beams enter and exit LUXC through a cylindrical section beryllium window. A schematic of the quasi-6-circle diffractometer at station 9.4 is shown in figure 3.5. The diffractometer is essentially a standard 4-circle ( $\delta$ ,  $\omega$ ,  $\chi$  and  $\phi$ ) system mounted on an horizontal  $\alpha$  table. Each circle has an angular resolution of 0.000125°. The  $\phi$  and  $\chi$  circles are used to position the sample, the  $\omega$  circle is used to rotate the sample about its surface normal. The  $\delta$  and  $\gamma$  circles are used to position the detector. The  $\gamma$ circle only has two possible settings: 0 or 15° (hence the quasi-6-circle nomenclature). This extra degree of freedom allows the accessibility of extra regions within reciprocal space. The entire diffractometer can be rotated using the  $\alpha$  table to independently fix the x-ray angle of incidence. The diffractometer operates under VME control of stepper and DC servo motors.



Figure 3.4: The Leicester University x-ray chamber (LUXC) coupled to the quasi-6-circle diffractometer at station 9.4 of the SRS, Daresbury



Figure 3.5: Schematic diagram of the 6-circle diffractometer on station 9.4 at the SRS, Daresbury

#### Sample alignment

The entire diffractometer is translated horizontally and vertically to align the centre of the rotation with the focused x-ray beam. After setting the zero position of the  $\alpha$  table and the detector angles  $\delta$  and  $\gamma$ , the sample is aligned with respect to the diffractometer. The  $\chi$  arc and the  $\phi$  circle (see figure 3.5) are optimised to minimise the precession of a laser beam reflected from the sample surface as the  $\omega$  circle (on which the  $\chi$  arc and  $\phi$ circle are mounted) is rotated. In this manner, the surface normal of the sample is aligned with the diffractometer to within 0.03°. The sample is then crystallographically aligned by measuring two Bragg x-ray reflections. Using the location of these Bragg reflections, a transformation between the crystal lattice frame of reference and the laboratory frame of reference is calculated (the UB matrix). This allows the diffractometer to be positioned directly in terms of reciprocal lattice co-ordinates of the sample. The sample surface is then aligned parallel to the x-ray beam and the sample translated horizontally within LUXC until the x-ray beam half cuts the sample. The pre-sample, post sample and detector slits are centred with respect to the beam by translating the slits through the x-ray beam and monitoring the detected intensity.

## 3.7 X-ray diffraction correction factors

In section 2.2.10 the intensity of a idealised Bragg reflection was calculated to be:

$$I_S(\mathbf{q}) = I_0 \left(\frac{r_0}{R_0}\right)^2 \left|F(\mathbf{q})\right|^2 \left(\frac{\sin^2 N_1 \pi h}{\sin^2 \pi h}\right) \left(\frac{\sin^2 N_2 \pi k}{\sin^2 \pi k}\right) \left(\frac{\sin^2 N_3 \pi l}{\sin^2 \pi l}\right)$$
(3.4)

To be able to compare the theoretical intensity with experiment, a number of correction factors need to be applied.

#### **3.7.1** The polarisation correction

To account for the polarisation of the x-ray beam, equation 3.4 needs to be multiplied by a polarisation factor, P. The polarisation factor of the beam can be decomposed into horizontal,  $P_{\text{hor}}$ , and vertical components  $P_{\text{ver}}$ :

$$P = xP_{\rm hor} + (1-x)P_{\rm ver},$$
 (3.5)

where x specifies the relative horizontal and vertical contributions to the total polarisation. For a six-circle diffractometer, the horizontal and vertical polarisation components are functions of the diffractometer position:

$$P_{\rm ver} = 1 - (\sin \delta \cos \gamma)^2 \tag{3.6}$$

$$P_{\rm hor} = 1 - (\sin\alpha\cos\delta\cos\gamma + \cos\alpha\sin\gamma)^2 \tag{3.7}$$

For a synchrotron source, the polarisation of the x-ray beam in almost entirely in the horizontal plane,  $x \approx 1$ , therefore:

$$P \approx P_{\rm hor} = 1 - (\sin \alpha \cos \delta \cos \gamma + \cos \alpha \sin \gamma)^2. \tag{3.8}$$

When  $\gamma = 0$ , equation 3.8 simplifies to:

$$P \approx 1 - (\sin \alpha \cos \delta)^2 = \sin^2 \delta + \cos^2 \alpha \cos^2 \delta$$
(3.9)

For scans in the horizontal plane  $\delta = 0$ ,  $P \approx 1 - (\sin \alpha)^2 = \cos^2 \alpha$ . For scans in the vertical plane  $\alpha = 0$ ,  $P \approx 1$ .

### 3.7.2 The Lorentz correction

Equation 3.4 assumes a perfectly monochromated and collimated x-ray beam and an idealised infinitesimal detector. In reality, the incident x-ray beam will be divergent and have a finite spread of wavelengths. A real detector will also accept an angular range of diffracted x-rays. In an experiment, the crystal is rotated about the surface normal

using the  $\omega$  circle until all the intensity from the Bragg peak (or Bragg rod in the case of diffraction from a 2-D surface) has been collected (a rocking scan). This measured quantity is the integrated intensity,  $I_{int}$ . The Lorentz correction factor,  $C_L$ , is a geometric correction term which accounts for how the diffracted Bragg peak is scanned through the detector. A comprehensive list of polarisation and Lorentz correction factors, for a variety of diffractometer geometries, can be found in the supporting manual to the ANA-ROD software [11].

### 3.7.3 The illuminated area correction

The active sample area is defined to be the illuminated area of the sample observed by the detector. To normalise the active area for all measurements, an area correction term,  $C_A$ , needs to be applied. This is a function of:

- the pre-sample slit settings (defining the dimensions of the incident beam);
- the incident x-ray angle,  $\beta_{in}$ ;
- the detector slit settings (defining the area viewed by the detector);
- and the detector angle,  $\delta$ .

A comprehensive list of area correction factors is given by Steadman [12].

## 3.7.4 The integrated intensity

The remaining correction is to fit a smooth curve to the background level and subtract this from the integrated intensity. After accounting for all the correction factors, the measured integrated intensity is proportional to:

$$I_{int}(\mathbf{q}) \propto I_0 \left| F(\mathbf{q}) \right|^2 P C_A C_L \tag{3.10}$$

Complex valued, theoretical structure factors,  $F(\mathbf{q})$ , can be calculated for a given sample and the squared modulus compared with the corrected integrated intensity:

$$\left|F(\mathbf{q})\right|^{2} = \frac{I_{int}(\mathbf{q})}{PC_{A}C_{L}}$$
(3.11)

## Chapter 4

# The atomic structure of $CaF_2-MnF_2-Si(111)$ superlattices

## 4.1 Introduction

Magnetically ordered epitaxial films, integrated with semiconductor substrates and layers are currently of great technological interest due to the development of "spintronics" and the synergy of magnetic and microelectronic systems. Of the possible materials being considered, manganese-based compounds are the prime candidates due to their high crystal quality and attractive magnetic properties, such as the observation of the giant Zeeman effect in superlattices containing Mn-based layers.

High-quality, nanoscale device production requires a fundamental understanding of the atomic ordering that occurs in the structures and at the interface between dissimilar materials during thin-film growth. Structural and magnetic characterisation are essential to predict and measure novel magnetic behaviour and determine whether such materials can be grown epitaxially and with minimal disorder on commercially available substrates such as silicon.

Recent reflection high energy electron diffraction (RHEED) studies have suggested that highly ordered, epitaxial manganese fluoride (MnF<sub>2</sub>) layers can be grown by molecular beam epitaxy (MBE) on a Si(111) substrate if a thin, strain-relieving, buffer layer ( $\approx$ 15 monolayers (ML)) of calcium fluoride (CaF<sub>2</sub>) is first deposited [13]. It has also been proposed [14] that below a critical thickness, very thin films of MnF<sub>2</sub> take on the fluorite structure of the CaF<sub>2</sub> buffer layers onto which they are deposited. A different structural arrangement may produce a different magnetic response.

Electron spin resonance (ESR) [15] and photo-luminescence (PL) [16] studies have discovered and identified magnetic differences between ultrathin (10 - 100 Å), thin (1000 -3000 Å) and bulk  $MnF_2$  films deposited on a  $CaF_2$  buffer layer on a Si(111) substrate. PL peak broadening and wavelength shifts, and fluorescence lifetime measurements, indicate a change in the crystal field of the  $Mn^{2+}$  ions between the bulk samples and thin films of  $MnF_2$ . This suggests that ultrathin films of  $MnF_2$  could be grown with novel, controllable magnetic properties simply by changing the thickness of the  $MnF_2$  film to be above or below the structural transition thickness ( $\approx$ 4-5 monolayers) from the bulk "rutile" state to the strained "fluorite" structure. Fluorescence EXAFS studies [17] have been used to investigate the local structure around the Mn atoms in highly ordered, epitaxial, MnF<sub>2</sub>– CaF<sub>2</sub> superlattices. Cathodo– and photo–luminescence experiments [18] have revealed a shift in the band maxima between thick (bulk-like) and thin MnF<sub>2</sub> films deposited onto a CaF<sub>2</sub> buffer layer, indicating structural differences.

We present the first high-resolution, synchrotron based, x-ray diffraction study to determine the 3-dimensional structure of  $MnF_2$ -CaF<sub>2</sub> superlattice samples. In-plane and out-of-plane measurements were made of the mature, buried CaF<sub>2</sub>-Si(111) interface, and the structure of  $MnF_2$  thin films within the superlattices.

## 4.2 The $MnF_2$ -Ca $F_2$ -Si(111) system

In order to understand how a complex, composite  $MnF_2-CaF_2-Si(111)$  superlattice is constructed, it is first necessary to consider the structure of the individual components. In this section we introduce the silicon, fluorite and rutile crystal structures (see table 4.1). Using knowledge of these basic building blocks, we then consider how the systems relate to each other crystallographically, and answer two basic questions: what are the possible orientations of fluorite on Si(111); and which planes of the rutile structure are closely lattice matched to fluorite.

Structure	Bravais lattice	Lattice vectors	Lattice angles
Silicon (bulk)	Cubic	a = b = c	$\alpha=\beta=\gamma=90^{\rm o}$
Silicon (surface)	Hexagonal	$a = b \neq c$	$\alpha=\beta=90^{\rm o},\gamma=120^{\rm o}$
Fluorite	Cubic	a = b = c	$\alpha=\beta=\gamma=90^{\rm o}$
Rutile	Tetragonal	$a = b \neq c$	$\alpha=\beta=\gamma=90^{\rm o}$

Table 4.1: Bravais lattices

#### 4.2.1 Bulk Silicon

Silicon crystallises in the face centred cubic, diamond structure. The lattice vectors which describe the cubic cell are:

$$\mathbf{A}_{1} = a_{0}\mathbf{i}$$
  

$$\mathbf{A}_{2} = a_{0}\mathbf{j}$$
  

$$\mathbf{A}_{3} = a_{0}\mathbf{k},$$
(4.1)

where the lattice constant of Si (at room temperature) is  $a_0 = 5.43072$  Å, and **i**, **j**, **k** are the Cartesian unit set of vectors. The corresponding reciprocal bulk cubic lattice vectors are:

$$\mathbf{B}_{1} = \frac{2\pi}{a_{0}}\mathbf{i}$$
$$\mathbf{B}_{2} = \frac{2\pi}{a_{0}}\mathbf{j}$$
$$\mathbf{B}_{3} = \frac{2\pi}{a_{0}}\mathbf{k},$$
(4.2)

## 4.2.2 Silicon(111)

#### Conventional, hexagonal surface cell

Figure 4.1 shows a plan view of the Si(111) surface. The in-plane vectors,  $\mathbf{a}_1$  and  $\mathbf{a}_2$ , (which lie parallel to the  $[1 \ 0 \ \overline{1}]$  and  $[\overline{1} \ 1 \ 0]$  bulk directions respectively) of the conventional surface cell are indicated in green.

$$\mathbf{a}_{1} = \frac{1}{2}(\mathbf{A}_{1} - \mathbf{A}_{3}) = \frac{a_{0}}{2}(\mathbf{i} - \mathbf{k})$$

$$\mathbf{a}_{2} = \frac{1}{2}(-\mathbf{A}_{1} + \mathbf{A}_{2}) = \frac{a_{0}}{2}(-\mathbf{i} + \mathbf{j})$$

$$\mathbf{a}_{3} = \mathbf{A}_{1} + \mathbf{A}_{2} + \mathbf{A}_{3} = a_{0}(\mathbf{i} + \mathbf{j} + \mathbf{k})$$

$$\begin{bmatrix} \mathbf{a}_{1} \\ \mathbf{a}_{2} \\ \mathbf{a}_{3} \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{A}_{1} \\ \mathbf{A}_{2} \\ \mathbf{A}_{3} \end{bmatrix}$$
(4.3)

$$|\mathbf{a}_1| = |\mathbf{a}_2| = \frac{a_0}{\sqrt{2}} = 3.8401 \text{\AA}, |\mathbf{a}_3| = \sqrt{3}a_0 = 9.40628 \text{\AA}.$$
 (4.4)



Figure 4.1: The conventional hexagonal (green) and non-conventional tetragonal (black) surface cells of the Si(111) surface (indexed in terms of the Si bulk vectors)

The corresponding reciprocal lattice vectors are:

$$b_{1} = \frac{2}{3}(B_{1} + B_{2} - 2B_{3}) = \frac{4\pi}{3a_{0}}(\mathbf{i} + \mathbf{j} - 2\mathbf{k})$$

$$b_{2} = \frac{2}{3}(-B_{1} + 2B_{2} - B_{3}) = \frac{4\pi}{3a_{0}}(-\mathbf{i} + 2\mathbf{j} - \mathbf{k})$$

$$b_{3} = \frac{1}{3}(B_{1} + B_{2} + B_{3}) = \frac{2\pi}{3a_{0}}(\mathbf{i} + \mathbf{j} + \mathbf{k})$$

$$\begin{bmatrix} \mathbf{b}_{1} \\ \mathbf{b}_{2} \\ \mathbf{b}_{3} \end{bmatrix} = \begin{bmatrix} \frac{2}{3} & \frac{2}{3} & -\frac{4}{3} \\ -\frac{2}{3} & \frac{4}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} \begin{bmatrix} \mathbf{B}_{1} \\ \mathbf{B}_{2} \\ \mathbf{B}_{3} \end{bmatrix}$$
(4.5)

$$|\mathbf{b}_1| = |\mathbf{b}_2| = \frac{4\pi}{3a_0}\sqrt{6} = 1.889\text{\AA}^{-1}, |\mathbf{b}_3| = \frac{2\pi}{3a_0}\sqrt{3} = 0.668\text{\AA}^{-1}.$$
 (4.6)

## Tetragonal surface cell

An additional, non-conventional, tetragonal surface cell is also indicated in black in figure 4.1:

$$\mathbf{c}_{1} = -2\mathbf{a}_{1} - \mathbf{a}_{2} = \frac{1}{2} \left( -\mathbf{A}_{1} - \mathbf{A}_{2} + 2\mathbf{A}_{3} \right) = \frac{a_{0}}{2} (-\mathbf{i} - \mathbf{j} + 2\mathbf{k})$$

$$\mathbf{c}_{2} = -\mathbf{a}_{2} = \frac{1}{2} \left( \mathbf{A}_{1} - \mathbf{A}_{2} \right) = \frac{a_{0}}{2} (\mathbf{i} - \mathbf{j})$$

$$\mathbf{c}_{3} = \mathbf{a}_{3} = \mathbf{A}_{1} + \mathbf{A}_{2} + \mathbf{A}_{3} = a_{0} (\mathbf{i} + \mathbf{j} + \mathbf{k})$$

$$\begin{bmatrix} \mathbf{c}_{1} \\ \mathbf{c}_{2} \\ \mathbf{c}_{3} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & -\frac{1}{2} & 1 \\ \frac{1}{2} & -\frac{1}{2} & 0 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{A}_{1} \\ \mathbf{A}_{2} \\ \mathbf{A}_{3} \end{bmatrix}$$

$$(4.7)$$

$$| \mathbf{c}_{1} |= a_{0} \sqrt{\frac{3}{2}} = 6.65125 \text{ Å}, | \mathbf{c}_{2} |= \frac{a_{0}}{\sqrt{2}} = 3.8401 \text{ Å}, | \mathbf{c}_{3} |= a_{0} \sqrt{3} = 9.40628 \text{ Å}.$$

$$(4.8)$$

The corresponding reciprocal lattice vectors are:

$$\mathbf{d}_{1} = \frac{1}{3}(-\mathbf{B}_{1} - \mathbf{B}_{2} + 2\mathbf{B}_{3}) = \frac{2\pi}{3a_{0}}(-\mathbf{i} - \mathbf{j} + 2\mathbf{k})$$

$$\mathbf{d}_{2} = (\mathbf{B}_{1} - \mathbf{B}_{2}) = \frac{2\pi}{a_{0}}(\mathbf{i} - \mathbf{j})$$

$$\mathbf{d}_{3} = \frac{1}{3}(\mathbf{B}_{1} + \mathbf{B}_{2} + \mathbf{B}_{3}) = \frac{2\pi}{3a_{0}}(\mathbf{i} + \mathbf{j} + \mathbf{k})$$

$$\begin{bmatrix} \mathbf{d}_{1} \\ \mathbf{d}_{2} \\ \mathbf{d}_{3} \end{bmatrix} = \begin{bmatrix} -\frac{1}{3} & -\frac{1}{3} & \frac{2}{3} \\ 1 & -1 & 0 \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} \begin{bmatrix} \mathbf{B}_{1} \\ \mathbf{B}_{2} \\ \mathbf{B}_{3} \end{bmatrix}$$
(4.9)
$$|\mathbf{d}_{1}| = \frac{2\pi}{3a_{0}}\sqrt{6} = 0.945\text{\AA}^{-1}, |\mathbf{d}_{2}| = \frac{2\pi}{a_{0}}\sqrt{2} = 1.636\text{\AA}^{-1}, |\mathbf{d}_{3}| = \frac{2\pi}{3a_{0}}\sqrt{3} = 0.668\text{\AA}^{-1}.$$
(4.10)

This non-conventional, rectangular surface cell is defined in advance to match the Si(111) surface to the rectangular unit cells of the  $CaF_2(111)$  and  $MnF_2(110)$  planes (which will be discussed in 4.2.5 on page 73). The stacking pattern of Si planes follows a 6-fold cyclical pattern (due to surface unit cell containing six (111) layers of atoms or three (111) bi-layers). The stacking sequence of (111) planes, starting with the top Si atom first (which we define to occupy the "A" positions) and extending into the bulk material, is: A, B, B, C, C, A. The "A", "B" and "C" positions in figure 4.1 are also known as the  $T_1$ ,  $T_4$  and the H<sub>3</sub> site respectively ("T" standing for "top", "H" standing for "hollow" and the numerical subscript referring to the co-ordination). The "A", "B", "C" labelling convention has been adopted here for simplicity.

#### **Real-space and Reciprocal-space co-ordinate transformations**

Real-space atomic positions can be described in terms of either the conventional or unconventional surface systems or the bulk co-ordinate system:

$$x\mathbf{a}_{1} + y\mathbf{a}_{2} + z\mathbf{a}_{3} = x^{*}\mathbf{c}_{1} + y^{*}\mathbf{c}_{2} + z^{*}\mathbf{c}_{3} = X\mathbf{A}_{1} + Y\mathbf{A}_{2} + Z\mathbf{A}_{3}$$

$$\begin{bmatrix} x & y & z \end{bmatrix} \begin{bmatrix} \mathbf{a}_{1} \\ \mathbf{a}_{2} \\ \mathbf{a}_{3} \end{bmatrix} = \begin{bmatrix} x^{*} & y^{*} & z^{*} \end{bmatrix} \begin{bmatrix} \mathbf{c}_{1} \\ \mathbf{c}_{2} \\ \mathbf{c}_{3} \end{bmatrix} = \begin{bmatrix} X & Y & Z \end{bmatrix} \begin{bmatrix} \mathbf{A}_{1} \\ \mathbf{A}_{2} \\ \mathbf{A}_{3} \end{bmatrix}$$

$$(4.11)$$

where lower and upper case letters indicate surface and bulk systems respectively. Similarly, a point in reciprocal-space can be described by either the conventional or unconventional surface systems or the bulk co-ordinate system:

$$h\mathbf{b}_{1} + k\mathbf{b}_{2} + l\mathbf{b}_{3} = h^{\star}\mathbf{d}_{1} + k^{\star}\mathbf{d}_{2} + l^{\star}\mathbf{d}_{3} = H\mathbf{B}_{1} + K\mathbf{B}_{2} + L\mathbf{B}_{3}$$

$$\begin{bmatrix} h & k & l \end{bmatrix} \begin{bmatrix} \mathbf{b}_{1} \\ \mathbf{b}_{2} \\ \mathbf{b}_{3} \end{bmatrix} = \begin{bmatrix} h^{\star} & k^{\star} & l^{\star} \end{bmatrix} \begin{bmatrix} \mathbf{d}_{1} \\ \mathbf{d}_{2} \\ \mathbf{d}_{3} \end{bmatrix} = \begin{bmatrix} H & K & L \end{bmatrix} \begin{bmatrix} \mathbf{B}_{1} \\ \mathbf{B}_{2} \\ \mathbf{B}_{3} \end{bmatrix}$$
(4.12)

The real-space transformation between any two of the three systems can be achieved by inserting equation 4.3 or 4.7 in equation 4.11. The reciprocal-space transformation between any two of the three systems can be achieved by inserting equation 4.5 or 4.9 in equation 4.12.

As an example consider the reciprocal space transformation between the bulk and conventional surface systems. Inserting equation 4.5 into equation 4.12 leads to:

$$\begin{bmatrix} h & k & l \end{bmatrix} \begin{bmatrix} \frac{2}{3} & \frac{2}{3} & -\frac{4}{3} \\ -\frac{2}{3} & \frac{4}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} \begin{bmatrix} \mathbf{B}_{1} \\ \mathbf{B}_{2} \\ \mathbf{B}_{3} \end{bmatrix} = \begin{bmatrix} H & K & L \end{bmatrix} \begin{bmatrix} \mathbf{B}_{1} \\ \mathbf{B}_{2} \\ \mathbf{B}_{3} \end{bmatrix}$$
$$\begin{bmatrix} h & k & l \end{bmatrix} \begin{bmatrix} \frac{2}{3} & \frac{2}{3} & -\frac{4}{3} \\ -\frac{2}{3} & \frac{4}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} = \begin{bmatrix} H & K & L \end{bmatrix}$$
$$\begin{bmatrix} h & k & l \end{bmatrix} \begin{bmatrix} \frac{2}{3} & \frac{2}{3} & -\frac{4}{3} \\ -\frac{2}{3} & \frac{4}{3} & -\frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} = \begin{bmatrix} H & K & L \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & \frac{1}{2} & 1 \\ -\frac{1}{2} & -\frac{1}{2} & 1 \\ 1 & 0 & 1 \end{bmatrix}$$
(4.13)

Table 4.2 lists the reciprocal-space conversions required for this work. The silicon bulk reflections are referenced using the bulk system; and the superlattice reflections converted from the non-conventional to the conventional surface system to allow comparison with other work.

### **4.2.3** $CaF_2$

 $CaF_2$  is a strongly ionic insulator that crystallises in a cubic close packed (CCP) structure (the fluorite structure). It is shown in figure 4.2 that the  $Ca^{2+}$  ions (4 per unit cell) occupy the corner and face-centred sites, and the  $F^{1-}$  ions (8 per unit cell) occupy the interstitial tetrahedral sites (the T sites). The Ca atoms are bonded to the 8 nearest F atoms while F atoms are bonded to the 4 nearest Ca atoms. Table 4.3 shows the atomic positions, within the conventional unit cell, in terms of the lattice vectors. The lattice constant of

Bulk	Conventional surface	Un-conventional surface
[H K L]	$[h \ k \ l]$	$[h^{\star} \ k^{\star} \ l^{\star}]$
[1 1 1]	[0 0 3]	[0 0 3]
[2 2 2]	[0 0 6]	[0 0 6]
[3 3 3]	[0 0 9]	[0 0 9]
[1 1 1]	[1 0 1]	[2 0 1]
[2 2 0]	[1 0 4]	$[\overline{2} \ 0 \ 4]$
	[1 0 <i>l</i> ]	$[\overline{2} \ 0 \ l^*]$
	[1 1 <i>l</i> ]	[3 Ī l*]

 Table 4.2: Conversions between bulk, conventional and non-conventional surface

 reciprocal-space scattering directions



Figure 4.2: The cubic fluorite structure unit cell (Ca - white, F - green)

Ca	F	
(0, 0, 0)	(0.25,0.25,0.25)	
$(0.5\;,0,0.5)$	(0.25,0.25,0.75)	
(0,0.5,0.5)	(0.25,  0.75,  0.25)	
(0.5,0.5,0)	(0.25,0.75,0.75)	
	(0.75,0.25,0.25)	
	(0.75,  0.25,  0.75)	
	(0.75,0.75,0.25)	
	(0.75,  0.75,  0.75)	

**Table 4.3:** Ca and F atomic positions within the fluorite unit cell (in terms of the bulk unit cell vectors)

CaF<sub>2</sub> (at room temperature) is  $a_{CaF_2} = 5.46295$  Å. The spacing between adjacent (111) planes (indicated in blue in figure 4.2) of Ca is  $b = \sqrt{3}a_{CaF_2}/3 = 3.1540$  Å.

### 4.2.4 The $CaF_2$ -Si(111) interface

The CaF<sub>2</sub> and Si(111) interface is a prototypical ionic insulator/covalent semiconductor system, of particular technological importance. The close lattice match (the lattice parameter of CaF<sub>2</sub> is 0.6% and 2.6% larger than Si at room temperature and the growth temperature,  $\approx 700^{\circ}$ C, respectively) means that high quality, epitaxial films of CaF<sub>2</sub> can be grown on Si(111). This offers the possibility of electronic device production such as: quantum dot (1D) and quantum well (2D) structures [19]; radiation-resistant electronics [20]; and infra-red sensor arrays [21]. The CaF<sub>2</sub>–Si(111) interface is also the starting point for device production of metallic films (Al and Cu) on CaF<sub>2</sub>–Si(111) [22].

The growth of  $CaF_2$  on Si(111) is, however, not simple and several different growth modes have been predicted [23]. Newly deposited  $CaF_2$  molecules can migrate across the sample surface interacting with other deposited  $CaF_2$  ad-molecules in the growing interface region and any area of the uncovered Si surface. The strength of interaction between the  $CaF_2$  molecules and the Si substrate, the mobility of the  $CaF_2$  molecules on the sample surface (determined by the substrate temperature) and the local morphology of the Si substrate (including factors such as vacancies and step edges) determine which mode of growth is energetically favourable. A number of growth regimes and atomically abrupt interfaces have been extensively studied using a wide range of techniques, including: atomic force microscopy (AFM) [24]; x-ray standing waves (XSW) [25]; x-ray photoelectron diffraction (XPD) [26]; x-ray diffraction and transmission electron microscopy (TEM) [27] [28] [29]; reflection high energy electron diffraction (RHEED) [30]; and STM [31].

Prior to CaF<sub>2</sub> growth, the substrate is annealed at 1250°C under UHV conditions. As the surface impurities are removed, a well ordered Si(111)-c(7x7) surface reconstruction is formed. The CaF<sub>2</sub> molecule is stable against thermal dissociation in the gas phase (enthalpy of dissociation  $\Delta H_{\text{diss}} = 8.9$  eV per molecule) and can be evaporated, under UHV conditions, from a molecular source onto the clean Si(111)-c(7x7) surface.

The CaF<sub>2</sub> molecule does not break up on contact with the Si substrate at room temperature. The Si(111)-c(7x7) reconstruction is retained and can be observed using electron or x-ray probes. 3-D islands growth occurs, leading to polycrystalline or amorphous films. As the substrate is heated to around 200°C, enough thermal energy is available to disrupt the Si(111)-c(7x7) reconstruction resulting in the formation of a type–A CaF<sub>2</sub>–Si(111) interface. In the type–A interface, the CaF<sub>2</sub> layers adopt the same crystal orientation as the Si substrate, while in the type–B interface the CaF<sub>2</sub> layers are rotated by 180° with respect to the Si(111) surface (the CaF<sub>2</sub> [112] axis is aligned with the Si [112] axis). Between 200°C and approximately 600°C, there is an increasing amount of thermal dissociation of F from the CaF<sub>2</sub> molecules to leave CaF. This bonds with Si to form energetically favourable F–Ca–Si bonds. The interface region under these conditions consists of Si–Ca–F + Si–F + Si–CaF<sub>2</sub> bonds and regions of local crystallinity exist. The growth regime is layer-by-layer (Frank-van der Merwe) growth. The maximum peak-to-peak height of the RHEED intensity oscillations is observed at 450°C. Above 600°C the  $CaF_2$  fully reacts with the Si substrate to form a well ordered crystalline type-B, non-stoichiometric Si-Ca-F interface layer. The excess F evaporates. As the interface layer forms, the underlying Si(111)-c(7x7) converts, via a number of (nx1) reconstructions, into the (3x1) reconstruction [27] where full activation is achieved. The unpaired electron of each Si surface atom is strongly bonded to Ca-F [32]. The growth of high quality CaF<sub>2</sub> films on top of the Si–Ca–F interface wetting layer can then be achieved via step-flow growth. RHEED measurements show no oscillations but a high intensity (approximately three times as large as before growth), indicative of a very flat morphology. At temperatures above approximately 200°C, the  $CaF_2$  islands eventually agglomerate to form a continuous, pseudomorphic film (of increasing quality with increased growth temperature) which fully covers the Si(111) surface. Above 800°C it is predicted that both of the fluorine atoms can be dissociated from the  $CaF_2$  molecule, resulting in a mixture of Ca, CaF and CaF<sub>2</sub> molecules near the interface region. This produces an interface layer with considerable roughness. Good quality device production would require two different growth conditions: high temperature growth to produce superior film morphology (homogeneity required for efficiency), and low temperature growth for reduced diffusion between the  $CaF_2$  films and other deposited films. The simplest method is to find an optimal temperature, but a much more successful "template" method has been developed which allows low temperature growth for the majority of the sample, whilst maintaining the high quality of films produced by high temperature growth. First, a buffer of 5-10 layers of  $CaF_2$  is grown at high temperature (above 600°C) forming a high quality, fully reacted type-B interface film which is accurately lattice matched to the Si substrate. This buffer layer then provides an ordered template for subsequent low temperature growth for the remainder of the  $CaF_2$  film and the other structures contained within the device. A review article by Olmstead [33] summarises the basic properties of epitaxial  $CaF_2$  films and the  $CaF_2$ -Si(111) interface, the methods used to characterise the system, and the technological potential of devices built from such materials.

Recent RHEED and AFM studies by Wang [34] and Horio [35] concentrated on attempts to grow defect-free, ultrathin  $CaF_2$  films on Si(111) at lower temperatures, a prerequisite

for other growth processes used in device production. Wang claims that films of comparable quality can be grown (without the template method mentioned above) at lower temperature in a layer-by-layer growth mode by carefully constraining the substrate to a narrow temperature window (430–470°C). Horio discusses equilateral triangular terraces and hollows on and within the CaF<sub>2</sub> films on Si(111), which can be utilised as templates for subsequent growth of other materials, leading to novel, nanoscale technology applications. Both studies show that further research is required to understand the different growth processes, the dynamics of the growing interface and to investigate the structure and stability of mature films used in device production. Horio suggests the possibility of the desorption of CaF<sub>2</sub> from the interface by electron stimulated desorption (ESD) [35]. This implies that x-ray methods rather than electron probes, such as RHEED, may be preferable as they will not influence the growth.

A number of research groups, including those led by Sokolov (Russia), Harada (Japan) and Lucas (UK), have identified four major interface configurations: type-A and type-B, both types exhibiting either a "short" or a "long" interface separation. Conversion from the type-A to the type-B interface can be achieved by annealing the sample - the required temperature and duration of the anneal being dependent on the thickness of the buffer layer. The "short" interface is metastable and transforms to the long interface [36] - the time period being dependent on the thickness of the structure. Figure 4.3 shows the type-A and type-B interfaces. The type-B interface separation, *a*, which is the distance from the top Si atom to the first Ca atom, has been reported by several groups in table 4.4. A number of other fundamental studies, to investigate the bonding configuration

	$a_{ m short}$	$a_{ m long}$	Reference
Lucas et al.	$2.348\text{\AA}$	4.108Å	[27]
Sokolov et al.	2.443Å	4.176Å	[36]
Harada et al.	2.428–2.433Å	3.808–4.208Å	[37]

 Table 4.4:
 Type-B interface characteristics

of calcium to silicon have also been carried out: Calcium Silicide (CaSi<sub>2</sub>) on Si(111) [38];



Figure 4.3:  $CaF_2$ -Si(111) interface

and silicon deposited onto a  $CaF_2$  substrate [39]. Investigations of the growth of  $CaF_2$  on substrates with different orientations, such as Si(100), have yielded ultrathin  $CaF_2$  films which have an inferior morphology. This has been attributed to the (111) plane having the lowest surface free energy.

### 4.2.5 MnF<sub>2</sub>

Antiferromagnetism exists in some metals, alloys and transition element salts when the material is cooled to below the Néel temperature. At low temperatures, an ordered array of atomic magnetic moments spontaneously forms, with alternate moments aligned in anti-parallel directions. In a perfect crystal there is, therefore, no net resultant magnetic moment in the absence of an applied field. In reality, crystal defects, spin canting and frustrated surface spins produce a small net field. Antiferromagnetic materials are repelled by an applied magnetic field: the magnetic susceptibility is a function of the applied field strength. For a fixed field strength, as the temperature increases, the magnetic susceptibility also increases, up to the Néel temperature (analogous to the Curie temperature for ferro- and ferri-magnetic materials). Above this critical temperature, approximately 67-72 K for  $MnF_2$ , the material becomes paramagnetic. In this state, the moments will align with an applied magnetic field, but thermal fluctuations destroy the magnetic ordering (the magnetic moments are randomly aligned) once the applied field is removed. Antiferromagnetic materials are conventionally used for a range of industrial uses that include GMR read-heads, to magnetically "pin" a ferromagnetic material via an exchange bias.

Figure 4.4 illustrates the conventional tetragonal unit cell for the "rutile" structure, exhibited by bulk  $MnF_2$ . Fluorine atoms occupy the hexagonal close packed (HCP) sites and manganese atoms occupy half of the distorted octahedral holes (fluorine and manganese atoms are coloured green and blue respectively). Octahedrally co-ordinated Mn atoms are bonded to the 6 nearest F atoms and trigonal planar co-ordinated F atoms are bonded to the 3 nearest Mn atoms. The lattice constants of MnF<sub>2</sub> are:  $a_0 = 4.8734$  Å;  $c_0 = 3.3099$  Å; and u = 0.305.



Figure 4.4: The tetragonal rutile structure unit cell (Mn - blue, F - green)

Mn	F	
(0, 0, 0)	(u, u, 0)	
(0.5, 0.5, 0.5)	(1 - u, 1 - u, 0)	
	(0.5 + u, 0.5 - u, 0.5)	
77.0-	(0.5 - u, 0.5 + u, 0.5)	

**Table 4.5:** Mn and F atomic co-ordinates within the rutile unit cell (u = 0.305)

A section of a (110) plane is indicated in figure 4.4 by blue lines. Figure 4.5 shows the bonding configuration of a  $MnF_2$  (110) layer: Mn and F atoms occupy the central layer and F atoms occupying layers above and below. For this reason each (110) plane is often referred to as a triple layer (TL). Adjacent triple layers are related by symmetry: a translation of half the unit cell in either of the in-plane axes [110] and [001] of the (110) plane. A new, tetragonal repeating unit cell, consisting of 3 triple layers, is defined in figure 4.6. This is defined in preparation for the section explaining how  $MnF_2$  stacks on

top of CaF<sub>2</sub>. The spacing between Mn layers in the (110) direction is  $a_0/\sqrt{2} = 3.44601$ Å. It has been shown that at high temperatures and pressures MnF<sub>2</sub> can crystallise into phases which are quite different to the rutile structure of bulk crystals of MnF<sub>2</sub> [40].



Figure 4.5: A cross section through the rutile (110) planes

# $4.2.6 \quad MnF_2-CaF_2$

The rutile and fluorite structures both have orthogonal basis sets of lattice vectors. Table 4.6 shows the in-plane epitaxial orientations and associated lattice mismatches (with respect to the Si structure) between the silicon, type–B fluorite and type–B rutile structures. Perpendicular to the interface, the silicon [111] direction is coincident with the [111] and [110] directions of type–B fluorite and rutile respectively. Figure 4.7 also illustrates the orientations of the rutile and fluorite structures.

# 4.3 $MnF_2$ -Ca $F_2$ -Si(111) Superlattices

A vast amount of research has been carried out to study superlattice systems. The majority of this work has focused on semiconductor superlattices, but relatively few



Figure 4.6: A stack of (110) rutile planes and new tetragonal unit cell

2	Direction	Length	Mismatch	Direction	Length	Mismatch
Si	[112]	6.65125 Å	0	[110]	3.8401 Å	0
CaF <sub>2</sub>	[112]	6.69071 Å	+0.6%	[110]	3.86289 Å	+0.6%
$MnF_2$	[110]	6.89203 Å	+3.6%	[001]	3.3099 Å	-13.8%

Table 4.6: In-plane, epitaxial relationships between the three crystal systems



Rutile (110)

# Fluorite (111)

Figure 4.7: Visualisation of the rutile and fluorite structures parallel to the interface, showing the tetragonal unit cells

have been devoted to studying ionic, wide band gap materials. Previous studies carried out by Sokolov [41] [42] concentrated on the growth and characterisation of  $CdF_2$ -CaF<sub>2</sub> superlattices on Si(111).

A number of experimental methods, including: fluorescent extended x-ray absorption and fine structure (EXAFS) [17]; atomic force microscopy (AFM) and x-ray diffraction [36] have recently been used to characterise the growth of  $CaF_2$  and  $MnF_2$  structures on Si(111). The results indicate that  $MnF_2$  films, thinner than five molecular layers, have a cubic (fluorite) structure like that of the buffer  $CaF_2$  layer. It is an example of a metastable phase stabilised by epitaxial growth. We note, however, that the atomic arrangement of growing layers at the surface can be significantly different from that of the "mature" interface, buried deep inside the final structure [43]. In attempting to understand the properties of hetero-structures, it is essential to measure the atomic arrangement of the complete assembly, rather than rely on the evidence of surface sensitive techniques alone. Figure 4.8 shows a schematic representation of the structure of the  $MnF_2-CaF_2-Si(111)$  superlattices studied here, including the  $CaF_2$  buffer and the structure of the  $MnF_2-CaF_2$  repeated unit.

# 4.4 Experimental

### 4.4.1 Aims of the experiment

The aim of this research was to determine the 3-dimensional structure of the superlattice samples using high resolution x-ray diffraction. Specifically, it was to determine:

- the type of CaF<sub>2</sub>-Si(111) interface (type-A or type-B, with a long or short separation), including the occupancies of the interface layers;
- the effect of the growth temperature of the buffer layer on the quality of growth;
- the lattice type and inter-layer spacing of the ultrathin MnF<sub>2</sub> layers within the repeated unit;
- the atomic separation between the ultrathin MnF<sub>2</sub> layers and CaF<sub>2</sub> layers within the repeated unit;
- if the predicted structural phase change of the MnF<sub>2</sub> layers can be observed with the samples provided.

# 4.4.2 Superlattice production

A series of  $MnF_2$ -CaF<sub>2</sub> superlattice structures, deposited on Si(111) substrates, were manufactured at the Ioffe Institute in St Petersburg, Russia. Si(111) wafers with miscuts of typically 0.05–0.12° towards either the [110] or [112] directions were loaded into the MBE chamber (see figure 4.9). After thermal annealing to remove the oxide contaminants,



Figure 4.8: A schematic representation of a superlattice structure

a distinct, well formed, Si(111)-c(7x7) reconstruction was observed using in-situ RHEED. Following the template method discussed in section 4.2.4 a pseudomorphic CaF<sub>2</sub> buffer layer (typically 15ML) was deposited at high temperature (701°C), forming a well-ordered, fully-reacted interface. Onto this buffer layer, the superlattice structure was then built up, each repeated unit within the superlattice containing ultrathin layers of  $MnF_2$  (1–5ML) and slightly thicker CaF<sub>2</sub> layers (5–15ML), deposited from separate CaF<sub>2</sub> and  $MnF_2$ molecular evaporators. Full details of the sample production are given elsewhere [36]. The final structures were then removed from the vacuum chamber and checked for perfection using AFM. The results (see figure 4.10) typically show terraces with a width of approximately 300nm (3000Å). Assuming that the terraces are a single layer of CaF<sub>2</sub> high (3.17Å), this corresponds to a miscut of approximately 0.06°. It is believed that the bright spots represent either large impurity clusters adsorbed on the sample surface following atmospheric exposure, or single layer island clusters of CaF<sub>2</sub> molecules, which form preferentially at the step edges. As higher coverage is achieved, the clusters grow in size and coalesce into single domain monolayer films.

Sections (10mm x 5mm) were then cleaved (along crystallographic directions) from the 3 inch wafers, carefully packaged. The samples were transported in air to our research laboratory, where they were stored under low vacuum ( $10^{-4}$ – $10^{-6}$ mbar) to limit further atmospheric degradation during the intervening weeks before the synchrotron experiments.

### 4.4.3 Experimental measurements

Table 4.7 lists the range of superlattices studied with x-rays at the ESRF.



Figure 4.9: The MBE chamber at the Ioffe Institute, St Petersburg



Figure 4.10: AFM image of sample 903

Sample	Repeated unit	Repeats	$CaF_2$ buffer	Substrate
860	$CaF_2 8ML/MnF_2 3ML$	1	4ML 1°C/8ML 701°C	Si(111)
863	$CaF_2 15ML/MnF_2 2ML$	10	7ML 1°C/8ML 701°C	Si(111)
864	$CaF_2 15ML/MnF_2 3ML$	10	7ML 1°C/8ML 701°C	Si(111)
902	$CaF_2 6ML/MnF_2 5ML$	6	7ML 102°C/5ML 812°C	Si(111)
903	$CaF_2 6ML/MnF_2 2ML$	6	7ML 10°C/5ML 812°C	Si(111)
904	$CaF_2 6ML/MnF_2 5ML$	10	7ML 102°C/5ML 812°C	Si(111)

 Table 4.7:
 Superlattice parameters

#### Measurements at the ID32 beamline, ESRF

The first allocation of beamtime was carried out at the ID32 beamline at the ESRF, using x-rays of energy 25 keV (0.496Å). Samples were mounted on a machined aluminium cylindrical sample holders using wax. They were then attached to a 4-circle (2+2) diffractometer operating in the vertical scattering geometry (see figure 4.11). The sample height and the protrusion of the sample holder from the goniometer were optimised using an optical leveller. A laser was used to align the sample surface to within 0.017 degrees (of the order of the sample miscut angle). The pre-sample, horizontal-gap slits were closed to 0.15 mm to produce a well collimated x-ray beam (the x-ray beam intensity is approximately constant in the vertical plane), which was used for crystallographic alignment of the sample using two Bragg peaks to calculate the "UB" orientation matrix. Alignment was verified by measuring two additional non-equivalent Bragg peaks. A lead shield was placed downstream from the sample to block the direct beam (see figure 4.11). By reducing the air-scattering, the background level of the detector was considerably reduced (from approximately 600 counts to 400 per second by the addition of the lead shielding).

Two sets of measurements were carried out on samples 863 and 864 (see table 4.7):

- Preliminary reflectivity scans along the (0 0 l) direction up to l = 8 (to encompass the Si(111) and Si(222) bulk peaks), probing the superlattice structure perpendicular to the plane of the interface (out-of-plane);
- Non-specular (1 0 l), (1 0 l), (1 1 l) and (1 1 l) CTR scans. Carried out to probe the superlattice structure out-of-plane and parallel to the plane of the interface (in-plane). This technique is routinely used to determine the in-plane structure of surface reconstructions.

Several periods of oscillations were observed in the reflectivity scans, each set produced by a different repeated distance within the superlattice sample (such as the interlayer spacings, the repeated unit thickness and the entire superlattice thickness). Interference between these sets of peaks means that the reflectivity scan is very sensitive to small changes in the structure and spacing of the layers, particularly in the vicinity of the Si(111) peak and the absent Si(222) peak. It was successfully demonstrated that the shortest period of oscillations in the reflectivity, caused by the thickness of the entire superlattice, could be experimentally resolved ( $\Delta l \approx 0.017$ ).



Figure 4.11: The four circle (2+2) diffractometer at ID32

#### Measurements at the UK CRG beamline XMaS (BM28), ESRF

The second beamtime was carried out at the UK Collaborating Research Groups (CRG) XMaS beamline (BM28) at the ESRF, using x-rays of energy 10 keV (1.24Å).

Suction caused by the rapid flow of air past a small aperture in the plate of the goniometer

was sufficient to firmly fix the sample to the 11-axis/4 circle Huber diffractometer, operating in a vertical  $\theta_v$ ,  $2\theta_v$  mode (see figure 4.12).

The pre-sample Huber slits (which define the size of the incident beam) were set to 1.5mm vertical gap and 2.5 mm horizontal gap. The detector slits (which define the detector resolution) were set to 1.5mm vertical gap and 2 mm horizontal gap.

An initial estimate for the values of  $\theta_v$  and  $2\theta_v$  at the Si(111) reflection can easily be calculated from Bragg's law:

$$n\lambda = 2d_{\mathrm{Si}(111)}\sin\theta_v \tag{4.14}$$

where  $\lambda$  and  $d_{\text{Si}(111)}$  are the x-ray wavelength and the distance between the Si(111) planes. For a wavelength of 1.24Å this gives  $\theta_v = 11.402^{\circ}$  and  $2\theta_v = 22.807^{\circ}$ . Nearby regions in reciprocal space can then be searched to find and accurately optimise upon the Si(111) Bragg peak.

Any misalignment may mean a gradual drift away from the  $(0 \ 0 \ l)$  rod as the reflectivity is scanned. To correct for misalignment errors, the reflectivity was split into a number of sections (this also allowed for a range of attenuation settings, maximising the detector count rate for enhanced statistics, whilst ensuring the detector didn't overload near Bragg peaks). Before each section of the reflectivity was scanned, horizontal  $\theta_h$  scans (which transversed the rod) were performed at the start and end to accurately locate the centre of the rod. The reflectivity could then be scanned, taking into account any misalignments which had been found from the transverse scans. A background scan, with  $\theta_h$  offset (to a background level), was recorded in order to allow normalisation of the reflectivity curve.

Technically, we measured a "ridge scan" (scanning along the top of the specular rod's "ridge"). To carry out a traditional reflectivity scan,  $\theta_v$  and  $2\theta_v$  are moved to their starting positions and a transverse  $\theta_h$  scan is completed. The integrated intensity from this scan forms a single value for the reflectivity.  $\theta_v$  and  $2\theta_v$  are then moved to their next positions and the process repeated, building up the reflectivity point by point. For our well defined and carefully aligned crystal surface, ridge scans produce reliable data [44]

and allow the rapid measurement of a large number of closely spaced oscillations in the superlattice's specular rod  $(0\ 0\ l)$ , a significant advantage over the traditional reflectivity method.



Figure 4.12: The 11-axis, 4 circle Huber diffractometer at XMaS

#### A Directs factor The Locont's reflectivity for or fillent

## 4.4.4 Data reduction

To compare the diffracted x-ray intensity with theoretical structure factor calculations, a number of "correction factors" need to be applied to the raw data:

- Beam intensity. The synchrotron storage ring is "topped-up" with electrons two or three times per day. Between fills the incident beam intensity decays with time as electrons are lost from the storage current. The pre-sample, ionisation chamber indicates the incident beam intensity, detector counts are normalised to this value.
- Sample degradation. Sample degradation may occur during the experiment caused by beam damage. To account for this factor, a standard scan is periodically repeated during the experiment. For our experiment, no degradation was observed.

- Attenuation corrections. To ensure that the detector doesn't overload in the vicinity of Bragg peaks (resulting in a non-linear response from the detector, and ultimately causing damage to the detector), thin attenuating films (typically aluminium or lead) are placed up-stream from the sample. To be able to compare scans with different attenuation, overlapping regions need to be scanned. These scans can then be multiplied by an appropriate attenuation factor to match up with the overlap from other scans.
- Background subtraction. A smooth curve is fitted to the background scans. This smooth curve can then be subtracted from the raw data, ensuring extra noise isn't introduced into the measured signal.
- Area of sample illuminated by the x-ray beam. The diffracted intensity will be proportional to the area of the sample illuminated by the x-ray beam. The raw data is multiplied by 1 for angles below the flooding angle  $\theta F$  (when the sample is "flooded") and by  $\sin \theta / \sin \theta_F$  for angles above  $\theta_F$ .
- Lorentz factor. The Lorentz reflectivity factor.  $1/\sin 2\theta$
- Polarisation. In a synchrotron source, the electrons orbit and are accelerated in the horizontal plane. The emitted x-rays are therefore heavily polarised in the horizontal plane. When the detector is located in the same plane as the polarisation (horizontal), the polarisation factor,  $P = \cos^2 \alpha$ . When the detector is moved vertically, out of the polarisation plane, the polarisation factor, P = 1.

A comprehensive list of Polarisation and Lorentz factors for a variety of diffractometer geometries can be found in supporting manual to the ANA-ROD software: "From beam time to structure factors" written by Elias Vlieg <sup>1</sup>.

Finally, to allow comparison between experiments using different x-ray wavelengths, the scattering angle  $2\theta$  is converted into perpendicular momentum transfer l (in terms of the

l

<sup>&</sup>lt;sup>1</sup>Download from: www.esrf.fr/computing/scientific/joint\_projects/ANA-ROD/home.htm

Si lattice parameter and the x-ray wavelength) via Bragg's law:

$$|\mathbf{q}| = \sqrt{H^2 |\mathbf{b}_1|^2 + K^2 |\mathbf{b}_2|^2 + L^2 |\mathbf{b}_3|^2} = \frac{4\pi}{\lambda} \sin\theta$$
(4.15)

For the reflectivity, H = K = 0:

$$L = \frac{4\pi}{|\mathbf{b}_3| \lambda} \sin \theta = \frac{2\sqrt{3}}{\lambda} a_{0(\mathrm{Si})} \sin \theta$$
(4.16)

# 4.5 Modelling the experimental data

### 4.5.1 Theoretical considerations

X-ray reflectivity is widely used to determine the structure of a wide range of twodimensional systems including: liquid crystals; Langmuir layers (amphiphilic molecules on a water surface); semiconductor surface reconstructions; and multilayers (amorphous) and superlattices (crystalline). The Fresnel equations, in conjunction with Snell's law, can be used to calculate the reflectivity from the electron density profile. In the "slab" method, a sample composed of different layers of atoms or molecules the sample is split into a number of constant electron density, vertically layered "slabs" (the electron density between slabs is assumed to vary smoothly). The kinematical scattering contributions from each of the slabs are calculated and combined (with appropriate phase terms) to predict the scattering from the entire sample. The Parratt formalism builds upon the kinematical approach by including multiple scattering. A full dynamical treatment is required to accurately model the diffracted radiation for angles at which the material scatters a significant percentage of the incident radiation. The "slab" method has been used successfully to determine the vertical structure of materials [45, 46], but gives no information about the structure in the horizontal plane. It is, therefore, of restricted value for materials which order pseudomorphically.

For ordered surface reconstructions which involve up to six layers, and show long range

ordering in the surface plane, it is normal to use an atomistic approach. In this, the complex valued scattering from all the atoms located in three dimensions within the layer is summed, and added (with an appropriate phase factor) to that of the bulk using the freely available ROD software. We extend this technique to superlattices, with up to 200 layers. Comparison would be made with the scattering vector aligned along the normal to the interface (reflectivity) and along the rods in reciprocal space with an inplane component (non-specular scattering). During the fitting of structural models for the superlattices to the measured scattering profile Grundmann independently developed an atomistic kinematic theory (AKT) to simulate the x-ray scattering using the positions of all the individual atoms within a strained superlattice structure. He compared the AKT method with a number of commercially available, computationally intensive, dynamical scattering software packages [47–51] and found that the 2-beam dynamical approximation methods failed to accurately model scattering from the superlattices at large scattering angles, away from Bragg reflections, providing justification for the use of semi-kinematical atomistic methods in these regimes. Powerful second and third generation synchrotron sources can now provide sufficient x-ray intensity to record scattering from the superlattice away from the Bragg peaks.

### 4.5.2 Structure factor calculation using ROD

We have developed an atomistic, semi-kinematical modelling technique in conjunction with the freely available ANA-AVE-ROD structure factor calculation software <sup>2</sup>. ROD has been used for many years to successfully refine structural models of atomic surfaces. Given input files containing the atomic co-ordinates of all the atoms in the bulk (".bul" file) and surface (".sur" file) unit cells, ROD uses expressions for the atomic form factors,

<sup>&</sup>lt;sup>2</sup>Download from: www.esrf.fr/computing/scientific/joint\_projects/ANA-ROD/home.htm

 $f_n$  to calculate the bulk, surface and total structure factors,  $F(\mathbf{q})$ .

$$F(\mathbf{q}) = \sum_{n} f_{n} \exp^{i(\mathbf{q}\cdot\mathbf{r}_{n})}$$

$$F(h,k,l) = \sum_{n} f_{n} \exp^{i(h\mathbf{b}_{1}+k\mathbf{b}_{2}+l\mathbf{b}_{3})\cdot(x_{n}\mathbf{a}_{1}+y_{n}\mathbf{a}_{2}+z_{n}\mathbf{a}_{3})}$$

$$F(h,k,l) = \sum_{n} f_{n} \exp^{2\pi i(hx_{n}+ky_{n}+lz_{n})}$$

$$(4.17)$$

The square modulus of the calculated complex valued structure factors can be compared with the real valued experimental measurements of the scattered x-ray intensity, which have been previously read into ROD. When the momentum transfer vector lies perpendicular to the sample surface, h = k = 0, the structure factor shown in equation 4.17 reduces to an expression for the reflectivity structure factors:

$$F(0,0,l) = \sum_{n} f_n \exp^{2\pi i l z_n}$$
(4.18)

The superlattice structure is constructed from only three basic building blocks: fluorite  $CaF_2$  triple layers; fluorite  $MnF_2$  triple layers; and rutile  $MnF_2$  triple layers. An expression for the structure factor of the entire sample can be calculated by summing (with appropriate phase factors) the contributions of the individual triple layers and combining them with the structure factor of the Si bulk.

The structure factors of individual triple layers (TLs) of fluorite  $CaF_2$  and fluorite and rutile  $MnF_2$  can be calculated by considering the number and location of the different atomic species within the tetragonal rutile and fluorite unit cells (shown in figure 4.7.

To illustrate the procedure for building the total structure factor for the entire sample, consider the simplified case of calculating the reflectivity structure factor (h = k = 0) from the contributions of individual triple layers of fluorite CaF<sub>2</sub>, fluorite MnF<sub>2</sub> and rutile MnF<sub>2</sub>:

CaF<sub>2</sub> (fluorite) 1TL

$$F_{\text{CaF}_2}(l) = 2(f_{\text{Ca}} + f_{\text{F}}e^{2\pi i lf} + f_{\text{F}}e^{-2\pi i lf})$$
(4.19)

 $MnF_2$  (fluorite) 1TL

$$F_{\rm MnF_2}^{\rm Fluorite}(l) = 2(f_{\rm Mn} + f_{\rm F}e^{2\pi i lg} + f_{\rm F}e^{-2\pi i lg})$$
(4.20)

 $MnF_2$  (rutile) 1TL

$$F_{\rm MnF2}^{\rm Rutile}(l) = 2f_{\rm Mn} + 2f_{\rm F} + f_{\rm F}e^{2\pi i lg} + f_{\rm F}e^{-2\pi i lg}$$
(4.21)

#### **Repeated unit**

The repeated unit consists of two parts: N triple layers (term 1) of  $MnF_2$ ; and P triple layers of  $CaF_2$  (term 2).

$$F_{\text{Repeat}}(l) = \underbrace{\left(\frac{1 - e^{2\pi i l N d}}{1 - e^{2\pi i l d}}\right) F_{\text{MnF}_2}(l)}_{1} + \underbrace{\frac{e^{2\pi i l (N-1)d + e}}{3} \left(\frac{1 - e^{2\pi i l P b}}{1 - e^{2\pi i l b}}\right) F_{\text{CaF}_2}(l)}_{2} \tag{4.22}$$

Term 3 in equation 4.22 is the required phase term to account for the intervening thickness of  $MnF_2$  layers, which have a total thickness of (N-1)d + e, between the start of the repeated unit and the start of the CaF<sub>2</sub> layers.

### Superlattice

The superlattice contribution can be constructed by combining Q repeated units:

$$F_{\text{Superlattice}}(l) = \left(\frac{1 - e^{2\pi i lQY}}{1 - e^{2\pi i lY}}\right) F_{\text{Repeat}}(l), \qquad (4.23)$$

where the repeated unit thickness Y = (N-1)d + e + (P-1)b + c.

### $CaF_2$ buffer

The  $CaF_2$  buffer consists of M triple layers:

$$F_{\text{Buffer}}(l) = \begin{cases} \left(\frac{1-e^{2\pi i lMb}}{1-e^{2\pi i lb}}\right) F_{\text{CaF}_2}(l) & \text{for the type-A interface,} \\ \left(\frac{1-e^{2\pi i lMb}}{1-e^{2\pi i lb}}\right) F_{\text{CaF}_2}(l) - 2F_{\text{F}}e^{-2\pi i lf} & \text{for the type-B interface.} \end{cases}$$
(4.24)

The subtracted term in equation 4.24 is required as the lower F component of the first  $CaF_2$  triple layer is absent in the type-B Si-CaF interface (see figure 4.3).

#### Si bulk

The Si bulk contribution is formed by a semi-infinite sum of unit cells:

$$F_{\text{Bulk}}(l) = \frac{F_{\text{unit}}}{1 - e^{-2\pi i l} e^{-\mu}},\tag{4.25}$$

where  $F_{\text{unit}}$  is the scattering from the Si surface unit cell and  $\mu$  is the attenuation factor for Si.

### Total structure factor

The total reflectivity structure factor for the complete ensemble can then be calculated:

$$F_{\text{Total}}(l) = F_{\text{Bulk}}(l) + e^{2\pi i la} F_{\text{Buffer}}(l) + e^{2\pi i lX} F_{\text{Super}}(l), \qquad (4.26)$$

where the buffer thickness X = a + (M - 1)b + c.

## 4.5.3 BUILD\_SUPERLATTICE

The parameters listed in table 4.8, which characterise each superlattice, can be split into two categories:

- Spatial parameters, a to h, which specify the interatomic distances within the superlattice and are assumed to be constant for all the samples;
- Structural parameters, *M*1 to *Structure*, which specify the type and number of layers within the superlattice and vary from sample to sample.

The initial values of the superlattice parameters are read into ROD and stored as variables. These variables are then output from ROD and read into our superlattice programme, BUILD\_SUPERLATTICE, which then generates a ".sur" surface file containing the 3-D co-ordinates of all the atoms within the superlattice, in terms of the non-conventional surface lattice vectors  $(\mathbf{c}_i)$  (defined in equation 4.10 and shown in figure 4.1 on page 63). The generated ".sur" file and the bulk file (containing the atomic positions of the Si substrate atoms) are then read in by ROD. The x-ray scattering from the bulk Si, the superlattice contribution and the combined superlattice and bulk contribution are then calculated by ROD. To attain agreement between the experimental and calculated scattered intensities, the superlattice variables are modified within ROD and output to BUILD\_SUPERLATTICE which generates a new ".sur" superlattice file. An iterative, interactive approach was employed to find a model which produced the best agreement between the square modulus of the calculated structure factors for the superlattice and experimental scattered x-ray intensity values. The frequently used chi-squared measurement of "goodness of fit" relied too heavily on fitting in the vicinity of the intense Bragg peaks.

#### Superlattice parameter justification

For extra flexibility, the interface distance (top Si to the first full layer of CaF<sub>2</sub>), a, has been split into two components,  $a_1 + a_2$ . This allows comparison with other models in which large interface separations (typically a = 4.2-4.6 Å) have been reported. Physically, this distance is too large for a Si-Ca bond (see Lucas [27]) and hence an extra CaF<sub>i</sub> (where i = 1 or 2) layer is needed between the top Si layer and the next CaF<sub>i</sub> layer. The occupancy

Variable	Property of superlattice
<i>a</i> 1	Spacing between top Si and 1st Ca
a2	Spacing between 1st Ca and 2nd Ca
b1	Spacing between Ca layers in high temp. buffer
b2	Spacing between Ca layers in room temp. growth
с	Spacing between Ca and Mn
d	Spacing between Mn layers
e	Spacing between Mn and Ca
f	Spacing between Ca and F ( $=d/4$ )
g	Spacing between Mn and F (Rutile) ( = $(1 - 2u)d$ )
h	Spacing between Mn and F (Fluorite) ( $=d/4$ )
M1	Number of $CaF_2$ layers in high temp. buffer
M2	Number of $CaF_2$ layers in room temp. buffer
N	Number of $MnF_2$ layers in repeated unit
Р	Number of $CaF_2$ layers in repeated unit
Q	Number of repeated units
Interface	Type–A or type–B
Structure	Rutile or fluorite $MnF_2$ layers

**Table 4.8:** The spatial (a to h) and structural (M1 to Structure) superlattice variables

of these first two  $CaF_i$  layers can be fitted within ROD. It has also expected that the initial  $CaF_2$  buffer layers grown at high temperature have larger out-of-plane spacings than those grown at room temperature (see table 4.11). To allow for this possibility we have used M1 layers separated by b1, and M2 layers separated by b2 for the high temp and room temp buffer layers respectively.

The out-of-plane stacking sequence for fluorite TLs follows a three layer sequence (i.e the 4th TL is identical to the 1st TL). Using this pattern, the in-plane atomic positions of any layer exhibiting the fluorite structure within the buffer or superlattice can be computed for a type–B interface by following the algorithm listed in table 4.9. Assuming that the rutile layers are lattice matched to the rectangular non-conventional surface cell, the four corner atoms will follow the same stacking sequence as the fluorite layers. The in-plane atomic positions of any layer exhibiting the rutile structure can be computed by following the algorithm listed in table 4.10. A convenient method of specifying the y-axis components (the [ $\overline{1}$   $\overline{1}$  0] bulk direction) of the atomic positions (which are multiples of 1/6 in terms of the rectangular surface cell, shown in figure 4.1 on page 63) is to use the modulo 6 numbering system, x%6 (6 mod 6 = 0, 7 mod 6 = 1, etc). Similar relationships between the *layer* number and the in-plane structure for type–A interfaces are also built into BUILD\_SUPERLATTICE.

Atom	x	У	z
F	0.0	$(2 \times layer + 4)\%6$	z-f
F	0.5	$(2 \times layer + 7)\%6$	z-f
Ca	0.0	$(2 \times layer + 0)\%6$	z
Ca	0.5	$(2 \times layer + 3)\%6$	z
F	0.0	$(2 \times layer + 2)\%6$	z+f
F	0.5	$(2 \times layer + 5)\%6$	z+f

Table 4.9: Stacking algorithm for type-B fluorite  $CaF_2$  or  $MnF_2$ 

Within the qth repeated unit, the vertical displacement (from the top Si atom) of the

Atom	x	У	z
F	0.0	$(2 \times layer + 3)\%6$	z-g
F	0.5	$(2 \times layer + 0)\%6 + 0.5$ -u	z
Mn	0.0	$(2 \times layer + 0)\%6$	z
Mn	0.5	$(2 \times layer + 3)\%6$	z
F	0.5	$(2 \times layer + 3)\%6$	z
F	0.0	$(2 \times layer + 3)\%6 + 0.5 + u$	z+g

Table 4.10: Stacking algorithm for type-B rutile  $MnF_2$ 

middle of the nth Mn layer is:

$$z = a1 + a2 + (M1 - 2) \times b1 + M2 \times b2 + (q - 1) \times (c + e)$$
  
+  $(Mn_{\rm T}[q] - q + 1) \times d + (Ca_{\rm T}[q] - q + 1) \times b2$   
+  $c + (n - 1) \times d$ , (4.27)

and the vertical displacement of the pth Ca layer is:

$$z = a1 + a2 + (M1 - 2) \times b1 + M2 \times b2 + (q - 1) \times (c + e)$$
  
+  $(Mn_{\rm T}[q] - q + 1) \times d + (ca_{\rm T}[q] - q + 1) \times b2$   
+  $c + (Mn_{\rm S}[q] - 1) \times d + e + (p - 1) \times b2,$  (4.28)

where  $Mn_{\rm S}[q]$  is the number of Mn layers in the *q*th repeated unit and  $Ca_{\rm T}[q]$  and  $Mn_{\rm T}[q]$ are the total number of Ca and Mn layers below the *q*th repeated unit respectively.

## 4.5.4 Resolution

The ultimate resolution in an x-ray measurement is limited by the energy resolution and the geometric convergence of the x-ray beam. The angular and energy dependence of the resolution,  $\delta L$ , of the perpendicular momentum transfer, L, (given in equation 4.16) can be found by partially differentiating with respect to  $\theta$  and  $\lambda$ .

$$dL = \frac{\partial L}{\partial \lambda} d\lambda + \frac{\partial L}{\partial \theta} d\theta$$

$$dL = -\frac{4\pi}{|\mathbf{b}_{3}| \lambda^{2}} \sin \theta d\lambda + \frac{4\pi}{|\mathbf{b}_{3}| \lambda} \cos \theta d\theta \qquad (4.29)$$

$$\left|\frac{dL}{L}\right| = \left|\frac{d\lambda}{\lambda}\right| + \cot \theta d\theta$$

The two terms in equation 4.29 represent the energy resolution and the beam convergence respectively. The energy / wavelength resolution is determined by the double-crystal Si(111) monochromator:

$$\left|\frac{d\lambda}{\lambda}\right| = 1.7 \times 10^{-4}.\tag{4.30}$$

The angular convergence of the x-ray beam,  $d\theta$ , can be calculated using geometrical considerations about the beamline:

$$d\theta = \frac{2 \times 10^{-3}}{27.3} = 7.326 \times 10^{-5} \text{rads.}$$
(4.31)

Equations 4.30 & 4.31 can be inserted into equation 4.29 to calculate the total resolution of the x-ray beam in terms of L:

$$dL = L(1.7 \times 10^{-4} + 7.326 \times 10^{-5} \times \cot \theta)$$
(4.32)

Equation 4.32 shows that the total resolution, dL, is a function of the incident angle. To simulate scattering measured on a "real" beamline, the calculated data is convoluted with "top-hat" functions of width dL, the width of which varies with L. As an example, consider the resolution at the Si(111) bulk peak (or Si(003) in terms of the surface vectors). The resolution at this angle ( $\theta_{003} = 11.404^{\circ}$  and L = 3) can be calculated, using equation 4.30, to be:  $dL = 1.6 \times 10^{-3}$ . A convolution of this type smears out sharp features in the calculated scattering.

### 4.5.5 Fitting procedure

A standard procedure was used throughout the analysis to model the superlattice structure. For brevity, this procedure is only shown for sample 863.

Initial estimates for the spatial superlattice parameters can be calculated using elastic continuum strain theory. It is believed that the  $CaF_2$  and  $MnF_2$  layers are lattice matched in-plane to the Si substrate. To accommodate the strain introduced into the  $CaF_2$  and  $MnF_2$  lattices, the lattices relax vertically. Given the in-plane lattice contractions/expansions, the vertical spacings of the  $CaF_2$  and rutile  $MnF_2$  layers can be calculated to a first approximation.

Consider a cuboid of dimension  $l_x \times l_y \times l_z$  with end face areas of  $A_x$ ,  $A_y$ ,  $A_z$ . If this volume of material is subjected to a set of forces, applied perpendicular to the cuboid faces, the new dimensions of the material can be calculated using elastic continuum theory:

$$\frac{\Delta l_x}{l_x} = \frac{1}{Y} \left[ \frac{F_x}{A_x} - \sigma \left( \frac{F_y}{A_y} + \frac{F_z}{A_z} \right) \right]$$

$$\frac{\Delta l_y}{l_y} = \frac{1}{Y} \left[ \frac{F_y}{A_y} - \sigma \left( \frac{F_x}{A_x} + \frac{F_z}{A_z} \right) \right]$$

$$\frac{\Delta l_z}{l_z} = \frac{1}{Y} \left[ \frac{F_z}{A_z} - \sigma \left( \frac{F_x}{A_x} + \frac{F_y}{A_y} \right) \right]$$
(4.33)

where  $\sigma$  is the Poisson ratio, Y is Young's modulus and  $\Delta l_x$ ,  $l_x$ ,  $F_x$ ,  $A_x$  are the change in length of the solid, the original length of the solid, the force applied and the end face area in the x-direction respectively. By applying interatomic, in-plane forces  $F_x$  and  $F_y$  to the CaF<sub>2</sub> and MnF<sub>2</sub> lattices, and setting  $F_z = 0$ , equation 4.33 can be simplified to yield the out-of-plane (z-direction) expansion/contraction of the atomic layers:

$$\frac{\Delta l_z}{l_z} = \frac{\sigma}{\sigma - 1} \left[ \frac{\Delta l_x}{l_x} + \frac{\Delta l_y}{l_y} \right]$$
(4.34)

Using a value of Poisson's ratio <sup>3</sup> for CaF<sub>2</sub>,  $\sigma_{CaF_2} = 0.28$ , gives an expansion of the CaF<sub>2</sub> layers in the z-direction of +0.46%. Applying similar arguments predicts a contraction of -6.3% in the z-direction for rutile MnF<sub>2</sub> layers which are lattice matched to Si.

 $<sup>^{3}</sup>$ www.almazoptics.com/homepage/CaF<sub>2</sub>.htm

	Bulk $z$ spacings	Strained $z$ spacings
Fluorite $CaF_2$ (20°C)	$3.154\text{\AA}$	3.168Å
Fluorite $CaF_2$ (700°C)	3.154Å	3.213Å
Rutile MnF <sub>2</sub>	3.446Å	3.23Å

**Table 4.11:** Initial estimates for the expansion / contraction of  $CaF_2$  and rutile  $MnF_2$  layers, in-plane lattice matched to Si(111), calculated using elastic strain continuum theory

Poisson's ratio calculations, strictly, are only applicable to continuous, bulk materials. At the atomic level, more complicated calculations (which take into account the individual bond strengths and charge distribution around atoms) are required to accurately simulate strain.

With initial estimates for the spatial superlattice parameters, the next step is to determine the structural superlattice parameters by measuring the location and spacing between the following sets of peaks in the experimental reflectivity data (see figure 4.13):

- central superlattice peaks produced by the average interlayer spacings
- major superlattice peaks produced by the thickness of repeated unit
- minor superlattice peaks produced by the total thickness of the superlattice

Spatial periodicity within the superlattice allows a number of structure factor terms to be grouped together and summed in geometric series. Here, we consider a simple model to explain the origin of the sets of oscillations in the experimental reflectivity measurements. Imagine a repeated unit containing N identical triple layers, each with a structure factor F and separated by a distance z (in terms of  $\mathbf{a}_3$ ). The structure factor for this simple repeated unit is:

$$F_{\text{Repeat}}(l) = \left(\frac{1 - e^{2\pi i N z l}}{1 - e^{2\pi i z l}}\right) F(l)$$

If we now sum over Q repeated units (each with a thickness of Z), the superlattice structure factor is:

$$F_{\text{Superlattice}}(l) = \left(\frac{1 - e^{2\pi i QZl}}{1 - e^{2\pi i Zl}}\right) F_{\text{Repeat}}(l)$$

$$F_{\text{Superlattice}}(l) = \left(\frac{1 - e^{2\pi i QZl}}{1 - e^{2\pi i Zl}}\right) \left(\frac{1 - e^{2\pi i Nzl}}{1 - e^{2\pi i zl}}\right) F(l).$$

$$(4.35)$$

The superlattice component then needs to be added to the complex valued expressions for the structure factors of the buffer layer and the bulk silicon substrate to calculate the total structure factor. The squared modulus of this quantity can then be calculated to compare with the experimentally determined reflectivity curves. In practise this will contain cross terms such as the superlattice structure factor multiplied by the complex conjugate of the buffer layer structure factor. The two dominant terms in the squared modulus of the total structure factor are: the squared modulus of the bulk silicon substrate; and the squared modulus of the superlattice, the latter term expressed as:

$$|F_{\text{Superlattice}}(l)|^{2} = \left(\frac{\sin^{2}\left(2\pi QZl/2\right)}{\sin^{2}\left(2\pi Zl/2\right)}\right) \left(\frac{\sin^{2}\left(2\pi 2Nzl/2\right)}{\sin^{2}\left(2\pi zl/2\right)}\right) |F(l)|^{2}$$
(4.36)

The origin of the factor of two in the denominator of the sine terms in the above equation is explained by replacing the exponential terms in equation 4.35 by sine terms:

$$\left(\frac{1-e^{iN\theta}}{1-e^{i\theta}}\right) = e^{\frac{i(N-1)\theta}{2}} \left(\frac{\sin(N\theta/2)}{\sin(\theta/2)}\right)$$
(4.37)

Equation 4.35 shows that the squared modulus of the superlattice term (and hence the total structure) is semi-periodic (as will be discussed later). The central superlattice peaks occur at:

$$l_{\text{central}} = \frac{M}{z},\tag{4.38}$$

where M = 1, 2, 3..., major superlattice peaks are separated by:

$$\Delta l_{\rm major} = \frac{1}{z} \frac{1}{(N-1)},\tag{4.39}$$

and minor peaks are separated by:

$$\Delta l_{\rm minor} = \frac{1}{Z} \frac{1}{(Q-1)}.$$
(4.40)
Figure 4.13 show Gaussian fits to the superlattice reflections near the Si(111) and Si(222) bulk Bragg peaks. The average spacing,  $d_{\text{Average}}$ , between the atomic layers within the entire superlattice structure can be calculated using the  $l_{\text{central}}$  values at which the major superlattice peaks occur and the order of the reflection, n:

$$d_{\text{Average}} = 9.40628 \times n/l_{\text{central}}$$

$$d_{(111) \text{ Average}} = 9.40628 \times 1/2.987 = 3.14907 \pm 0.0005\text{\AA}$$

$$d_{(222) \text{ Average}} = 9.40628 \times 2/5.9829 = 3.14439 \pm 0.0005\text{\AA}$$

$$(4.41)$$

The systematic absence of the forbidden Si(222) bulk reflection (apart from a sharp, higher order reflection component) means that kinematical scattering theory is valid in this region. Dynamical effects which could distort the position of the superlattice peak will be negligible. For this reason, it is assumed that the measurement of the (006) superlattice peak will yield a more accurate value for the average superlattice spacing rather than near the (003) peak.



Figure 4.13: Gaussian fit to the central superlattice peaks of sample 863 near the Si(111) and Si(222) bulk peaks to determine the average interatomic spacing within the superlattices

Let the *n*th measured peak be identified as peak number  $m_n$  and be located at an *l*-value of  $l_{m_n}$  (if every peak could be measured  $m_n$  would be identical to *n*, but destructive interference within the measured reflectivity meant that it wasn't possible to accurately measure all the superlattice peaks). Three methods were employed to determine the "average" spacing between oscillations:

• Measure the distances between adjacent peaks and average the result:

Peak separation<sub>average</sub> = 
$$\frac{1}{N-1} \sum_{n=2}^{n=N} \frac{l_{m_n} - l_{m_{n-1}}}{m_n - m_{n-1}}$$
 (4.42)

• Measure the distances from the first peak to each of the other peaks. Divide each distance by the number of peaks between the two measured peaks. Repeat this procedure for all the peaks in turn:

Peak separation<sub>combi</sub> = 
$$\frac{N(N-1)}{2} \sum_{i=1}^{i=N-1} \sum_{n>i}^{n=N} \frac{l_{m_n} - l_{m_{n-i}}}{m_n - m_{n-i}}$$
 (4.43)

where N is the total number of measured peaks.

• Linear regression of the peak position versus the peak number.

The "combination" method gives a better estimation than the "average" method for the oscillation spacing if a small number of peaks are displaced from their ideal positions. Table 4.12 lists a simplified set of peak measurements. All the peaks are separated from each other by 1 unit, apart from the last, which is purposely separated by 2 units.

The "averaging" method in equation 4.42 gives a peak separation of 1.125 units, whereas the "combination" method in equation 4.43 gives a separation of 1.064 units, much closer to the "true" value of 1 unit. A plot of  $l_{m_n}$  versus  $m_n$  would show the last peak measurement to be spurious. For large data sets, where human intervention would be excessively time intensive, the "combination" method is preferred to the "averaging" method. In determining the peak spacings for the reflectivity data, very similar results were produced by the three methods mentioned, primarily due to the high periodicity of the peaks. To illustrate the periodicity, the peak position was plotted against the peak number and the average major peak separation determined by linear regression. Figure 4.14 shows that for sample 863 the major peak separation is  $0.187 \pm 2 \times 10^{-4}$ . This equates

n	$m_n$	$l_{m_n}$	
1	1	1	
2	2	2	
3	3	3	
4	5	5	
5	6	6	
6	7	7	
7	8	8	
8	10	10	
9	11	12	

**Table 4.12:** A simple set of peak measurements to compare the "averaging" and"combination" methods of determining the peak separations

to a thickness for the repeated unit of approximately 50.3 Å. Given that the spacings for  $CaF_2$  and  $MnF_2$  are of the order of 3.15Å, the number of layers within the repeated unit can be calculated to be 16 or 17.

This procedure can then be repeated for the minor peaks. Figure 4.15 shows that the average minor peak separation is  $0.01722 \pm 2 \times 10^{-5}$ . This equates to the overall thickness of the superlattice and buffer structure being 546.2 Å.

The values for the average interlayer spacing, the average repeated unit thickness and the thickness of the buffer layer and the superlattice section give starting points for the simulation parameters. Other factors which need to be taken into account for the simulation are the types of structure within the  $MnF_2$  layers (rutile or fluorite), the interface type (type-A or type-B), and the interface distance a.

In the following section, theoretical fits are shown to the experimental reflectivity for three samples (860, 863 and 864) and non-specular  $(1 \ 0 \ l)$ ,  $(\overline{1} \ 0 \ l)$  and  $(1 \ 1 \ l)$  rods for sample 863.



**Figure 4.14:** Linear fitting of the major superlattice peaks of sample 863 to determine the average spacing between major superlattice peaks and hence calculate the superlattice repeated unit thickness



Figure 4.15: Linear fitting of the minor superlattice peaks of sample 863 to determine the average spacing between minor superlattice peaks and hence calculate the thickness of the entire superlattice

Simulations with the spatial parameters listed in table 4.13 were found to fit for all the samples. Figures 4.16 & 4.17 show final models for the type–B interface structure and the repeated unit structure respectively.

Parameter	Value		
a1	$1.95 \pm 0.1 \text{\AA}$		
a2	$2.3{\pm}0.1{ m \AA}$		
<i>b</i> 1	$3.168{\pm}0.005{ m \AA}$		
b2	$3.161 \pm 0.005 \text{\AA}$		
c = d	$3.03{\pm}0.005{ m \AA}$		
e = b2	$3.161 \pm 0.005$ Å		
f1	b1/4		
f2	b2/4		
g	$0.39 \times d$		

 Table 4.13:
 Superlattice fit parameters

#### Roughness

The calculated scattering for all the fits are from ideal superlattice samples, that is, from structures with perfect, abrupt boundaries between dissimilar materials, no inter-species diffusion and a perfect stacking arrangement for all the layers. The discrete, atomistic nature of the method limits the smearing out of the electron density in proximity to the interface regions, employed in the slab method calculations (a smooth, mathematical function, such as a Gaussian or Lorentzian is used to model the decay of one species into the next dissimilar structure). Within our theoretical framework, we have experimented with allowing inter-diffusion between the layers (i.e  $(MnF_2)_x$  and  $(CaF_2)_{1-x}$  at the interface), but found no significant improvement to the fits. This indicates complete or almost complete layers were formed before the next material was grown on top.



# **Repeated unit structure**

Figure 4.16: Final repeated unit structure (blue - manganese, white - calcium, green - fluorine)



# Interface structure

Figure 4.17: Final type-B interface (red - silicon, white - calcium, green - fluorine)

# 4.6 Experimental Data and Theoretical fits

There are two major objectives of the experiment:

- To determine the  $CaF_2$ -Si(111) interface structure;
- To establish the structure and spacing of the MnF<sub>2</sub> layers within a representative range of CaF<sub>2</sub>-MnF<sub>2</sub>-Si(111)superlattices.

#### 4.6.1 $CaF_2$ -Si(111) interface structure

The first goal of our research is to investigate the structure of the  $CaF_2$ -Si(111) interface and compare with the models predicted by Sokolov [36], Harada [37], Olmstead [33] and Lucas [28]. Our x-ray measurements and analysis determined the structural parameters for sample 860 to be:

Fluorite 
$$MnF_2, M1 = 7, M2 = 3, [3 \text{ TL } MnF_2 + 7 \text{ TL } CaF_2] \times 1$$

Since sample 860 contains a single repeated unit, the relatively few layers within the superlattice means that the total scattering is sensitive to the structure of the interfacial layers. Small changes in the interface separation or the layer occupancies produce measurable differences in the scattering. A single scaling factor is used for each sample, rather than applying different factors to the Si(111) and Si(222) regions. Figures 4.18 to 4.22 show experimental reflectivity measurements (red) and fits calculated by ROD and BUILD\_SUPERLATTICE (blue). Figure 4.18 shows the differences in scattering near to the Si(222) peak produced by superlattices containing rutile (green curve) or fluorite (blue curve)  $MnF_2$  layers. The agreement between experimental and the calculated intensity shows that the ultrathin layers of  $MnF_2$  in sample 860 exhibit the fluorite structure. The discrepancy shown in figure 4.19 between the calculated and the experimental reflectivity for very small values of L is explained by the break down of the kinematic method near to

the  $(0\ 0\ 0)$  Bragg peak. In this region, a full dynamical treatment is required to accurately model the experimental data.



Figure 4.18: Experimental reflectivity measurements of sample 860 (red), and calculated reflectivities showing the differences in scattering strength near the Si(222) peak for superlattices containing rutile  $MnF_2$  layers (green) and fluorite  $MnF_2$  layers (blue). This shows that sample 860 contains fluorite  $MnF_2$  layers

#### Interface type

The experimental (1 0) CTR data (red) for sample 863 in figure 4.23 shows bulk Si peaks at L = -5, 1 and 4 and superlattice peaks at L = -7, -4, -1, 2 and 5. In the type-A interface (green - displaced for clarity), theory predicts that the superlattice peaks coincide with the bulk peaks at L = -5, -2, 1 and 4. In the type-B interface (blue), the superlattice is rotated by 180° with respect to the Si substrate. This produces theoretical superlattice peaks at L = -7, -4, -1, 2, which coincide with the experimental superlattice peaks. This conclusively shows that all the samples measured had a type-B interface (which is predicted at high growth temperature for the CaF<sub>2</sub> buffer layer). This shows the flexibility of x-ray measurements and the atomistic modelling technique which can predict out-of-plane and in-plane scattering.



Figure 4.19: Experimental reflectivity measurements (red) of sample 860, for low L values and a simulated fit (blue)



**Figure 4.20:** Experimental reflectivity measurements (red) of sample 860, near to the Si(111) peak and a simulated fit (blue)



Figure 4.21: Experimental reflectivity measurements (red) of sample 860, near to the Si(222) peak and a simulated fit (blue)



Figure 4.22: Experimental reflectivity measurements (red) of sample 860, near to the Si(333) peak and a simulated fit (blue)



Figure 4.23: Scattering around the (1 0) non-specular rod for sample 863. The red curve shows the calculated intensity for a type–B interface and the green curve shows the calculated intensity for a type–A interface (displaced for clarity). The peaks at L = -5, 1 and 4 are produced by the bulk Si

#### Interface spacing and occupancies

Using realistic values for interface parameters listed in table 4.13 we obtained a theoretical reflectivity which matched all the major features of the experimental measurements (predominantly fitting to the experimental data for sample 860, which was sensitive to the interface region). However to achieve a greater agreement, we used chemical bonding considerations and allowed the occupancy levels for the first few layers to vary. An occupancy of one third for the first CaF layer is sufficient to satisfy the dangling bonds of the Si(111) surface.

The distance from the top Si atom to the Ca atom within the first CaF layer, a1, was found to be  $a1 = 1.95\pm0.1$ Å. There is a significant difference between this value and the measurements carried out by Olmsted (a1 = 2.15Å, determined using MEIS [33]) and Lucas ( $a1 = 2.3\pm0.1$ Å, determined using XRD [28]). However, if we consider the full interface distance for the long interface structure (a1 + a2) agreement is reached with the other groups (see table 4.14). We found an occupancy of  $0.45\pm0.2$  for the first CaF layer compared to Lucas's  $0.46\pm0.2$ . For the spacing between the first CaF layer and the next CaF<sub>x</sub> (where x=1 or 2) layer we found  $a2 = 2.3\pm0.1$ Å which compares to Lucas's value of  $a2 = 2.2\pm0.1$ Å. This distance is physically too small to fit a F layer between the first CaF and second CaF<sub>x</sub> layers (the Ca – Ca separation within a CaF<sub>2</sub> film is approximately 3.17Å). For this reason we assumed the second layer to also be CaF (x = 1), with an occupancy of  $0.65\pm0.2$ Å (identical to that of Lucas's model). Small displacements of the F and the top Si atoms were tested, but no improvement in the fit to the experimental data was observed.

A summary of the  $CaF_2$ -Si(111) interface characteristics for the five studies are listed in table 4.14. Note that a1 and the short and long interface distances quoted in table 4.14 have been converted to distances measured from the top Si atom rather than the middle of the top Si bilayer (used by other authors). After growth, both Lucas and Yakovlev [52] showed that the "short" type–B interface is meta-stable and converts to the stable "long" type-B interface when annealed or after prolonged periods (several weeks) of atmospheric exposure. Photoemission experiments [53] showed that exposure of  $CaF_2$ films to an atmospheric pressure of oxygen (and to a lesser extent, water vapour) caused a major change in the Si–Ca bond whilst the average local crystal structure of the entire film (measured using photoelectron diffraction) is unchanged. The agreement between our value for a1 + a2 and the "short" and "long" interface separations listed in table 4.14 shows that all the samples we measured were of the "long" type-B interface. This is to be expected, as several weeks elapsed between production and measurement of the superlattice samples (during which time they were stored under low vacuum conditions). The mechanism for the "short" to "long" transformation is still not fully understood. Sokolov proposed that the conversion rate is also increased by the presence of point defects within the  $CaF_2$  film.

	Group					
Parameters	This work	Lucas [28]	Sokolov [36]	Harada [37]	Olmstead [33]	
<i>a</i> 1	$1.95\pm0.1$ Å	$2.3{\pm}0.1\text{\AA}$			$2.15\text{\AA}$	
a2	$2.3{\pm}0.1\text{\AA}$	$2.2{\pm}0.1\text{\AA}$				
a1 + a2	4.25±0.2Å	$4.5{\pm}0.2\text{\AA}$				
Occ. 1st CaF	$0.45\pm0.2$ Å	$0.46{\pm}0.2\text{\AA}$				
Occ. 2nd CaF	$0.65 \pm 0.2$ Å	$0.65\pm0.2$ Å				
short		2.41Å	$2.51 \text{\AA}$	2.48Å	2.31Å	
long	4.25Å	4.5Å	4.21Å	4.19Å		

Table 4.14: Summary of the  $CaF_2$ -Si(111) interface characteristics

# 4.6.2 The structure of the $MnF_2$ layers within the superlattice repeated unit

Samples 863 and 864 are useful to understand the structure of the repeated unit. Our x-ray measurements and analysis determined the structural parameters for sample 863 to be:

Fluorite  $MnF_2$ , M1 = 7, M2 = 7, [3 TL  $MnF_2 + 14$  TL  $CaF_2$ ] × 2 + [2 TL  $MnF_2 + 14$  TL  $CaF_2$ ] × 8

Similarly, the structural parameters for sample 864 were found to be:

Fluorite  $MnF_2$ , M1 = 7, M2 = 6, [3 TL  $MnF_2 + 14$  TL  $CaF_2$ ] × 4 + [4 TL  $MnF_2 + 14$  TL  $CaF_2$ ] × 6

Samples 863 and 864 are useful to understand the structure of the repeated unit. The scattering from such samples is dominated by the contribution from the ten repeated units within each sample. Measurements of the repeated unit thickness and the central superlattice peaks for two similar samples differing in structure only by an additional  $MnF_2$  layer in each repeated unit (samples 863 and 864 have 2 and 3 TLs of  $MnF_2$  respectively), coupled with knowledge of the number of each type of layers within the repeated unit, leads to two simultaneous equations with two unknowns (the Ca–Ca spacing, b2 and the Mn-Mn spacing, d). The solution of which gives the required thickness of CaF<sub>2</sub> and MnF<sub>2</sub> layers within the repeated unit.

The Ca–Ca spacings found from our analysis were b1 = 3.168Å (within the high temperature buffer layer) and b2 = 3.161Å for the remaining room temperature growth repeated unit layers. These compare with values of  $3.17\pm0.008$ Å reported by Lucas,  $3.19\pm0.02$ Åfound by Yakovlev and Sokolov and 3.174Å reported by Harada.

The interlayer Mn–Mn spacing was found to be  $3.03\pm0.005$ Å. This compared to the value of  $3.05\pm0.005$ Å for fluorite MnF<sub>2</sub> layers found by Sokolov using RHEED. In his model,



**Figure 4.24:** Experimental reflectivity measurements (red) of sample 863, near to the Si(111) peak and a simulated fit (blue)



Figure 4.25: Experimental reflectivity measurements (red) of sample 863, near to the Si(222) peak and a simulated fit (blue)



Figure 4.26: Experimental  $(1 \ 0 \ L)$  non-specular rod measurements (red) of sample 863, showing the superlattice peak at L = 2, and a simulated fit (blue)



Figure 4.27: Experimental  $(1 \ 0 \ L)$  non-specular rod measurements (red) of sample 863, showing the bulk Si peak at L = 4 and the central superlattice peak at L = 5, and a simulated fit (blue)



Figure 4.28: Experimental  $(\overline{1} \ 0 \ L)$  non-specular rod measurements (red) of sample 863, showing the bulk Si peak at L = 1, and a simulated fit (blue)



Figure 4.29: Experimental  $(\overline{1} \ 0 \ L)$  non-specular rod measurements (red) of sample 863, showing the central superlattice peak at L = 4 and the bulk Si peak at L = 1, and a simulated fit (blue)



Figure 4.30: Experimental  $(1 \ 1 \ L)$  non-specular rod measurements (red) of sample 863, showing the coincidence of the central superlattice peak and the bulk Si peak at L = 3, and a simulated fit (blue)



Figure 4.31: Experimental reflectivity measurements (red) of sample 864, near to the Si(111) peak and a simulated fit (blue)



**Figure 4.32:** Experimental reflectivity measurements (red) of sample 864, near to the Si(222) peak and a simulated fit (blue)

Sokolov assumes the Ca–Mn and Mn–Ca spacings (c = e = 3.15Å) to be an average of the Ca–Ca and Mn–Mn spacings. However, a better fit to the experimental data reported here was found by setting the spacing between Ca and Mn (c) to be equal to the Mn–Mn spacing (d) and the spacing between Mn and Ca (e) to be equal to the Ca–Ca spacing (b2). Sokolov also used two methods to estimate the interlayer spacing for fluorite MnF<sub>2</sub>, using the ionic radius and the ionic volume. The former method gives a spacing of 2.69Å, the latter a value of 3.07Å; the experimental results producing a closer fit to the ionic volume calculation. They also measured much thicker MnF<sub>2</sub> films (approx 20 ML) and found the Mn–Mn interlayer spacing to be  $3.47\pm0.005$ Å, which is very close to the spacing between (1 1 0) planes of bulk MnF<sub>2</sub>. This is consistent with a structural transition from the rutile structure of bulk MnF<sub>2</sub> to the fluorite structure of ultrathin MnF<sub>2</sub> films.

Confirmation of the fluorite structure for ultrathin  $MnF_2$  layer is also provided in our reflectivity data by measurement near to the systematically absent Si(222) bulk peak. Our calculations in figure 4.36 show that superlattices with rutile  $MnF_2$  layers scatter approximately 10 times more intensely near the Si(222) bulk peak than an identical superlattice with fluorite  $MnF_2$  layers. All the superlattices measured, containing  $MnF_2$  films of varying thickness (2–5ML), adopted the rutile structure. The only indication of a fluorite-rutile structural transition was with sample 902, which contained a 5ML thick  $MnF_2$  film within the repeated unit. In this case, the average Mn-Mn spacing (3.07±0.005Å was found to be slightly larger than standard. This gave a distance from the last Ca atom to the top Mn atom of 5 × 3.07Å = 15.35Å (5  $MnF_2$  layers in repeated unit). Assuming the first four  $MnF_2$  layers had the standard spacing of 4 × 3.03Å = 12.12Å, this gives a thickness for the last layer of 3.23Å, indicating that the structural transition may be occurring between 4 and 5 ML of  $MnF_2$ .

# 4.7 Discussion

#### 4.7.1 Growth quality of superlattice samples

Samples 860, 863 and 864 all have buffer layers grown at high temperature (701°C, see table 4.7). The reflectivity and in-plane CTR scans show sharp, well formed major and minor superlattice peaks. Conversely, samples 902, 903 and 904, which have buffer layers grown at higher temperature (812°C), show broader, less well defined, major superlattice peaks (see figure 4.33). This indicates a greater non-uniformity within the repeated units, either a greater diversity in the numbers of each type of layer within the repeated units, or a greater degree of disorder. As discussed in section 4.2.4, buffer layers grown at higher temperature can contain Ca, CaF and CaF<sub>2</sub> species, which leads to inhomogeneity and inherent roughness at the CaF<sub>2</sub>-Si(111) interface. The buffer layer acts as a template for subsequent low temperature growth of the repeated units. Ordering within the repeated units is determined by the buffer: a rough starting surface, with small domain size limits the crystalline quality of the repeated units. For these reasons, our results indicate a large degree of ordering within the superlattices containing a high-temperature buffer layer (701°C).



**Figure 4.33:** Experimental reflectivity measurements for samples 863 (blue), 864 (cyan), 902 (red), 903 (green) and 904 (black), near to the Si(222) peak

#### 4.7.2 An evaluation of the atomistic semi-kinematical technique

The flexibility of the atomistic semi-kinematical technique is its ability to calculate the out-of plane (reflectivity) and the CTR measurements. Traditional kinematical "slab" methods that use the electron density profile normal to the surface (involving smoothing functions to simulate the roughness of the structures) have been highly successful in determining the out-of-plane structure of superlattices, but provide no information about the structure of the material in-plane. In our study, the calculations yielded important in-plane information such as: the type of interface (type-B); and the fact the  $CaF_2$  layers were epitaxial to the Si(111) substrate.

The sensitivity of the technique is illustrated by its ability to accurately determine the exact number and type of layers within the superlattice repeated unit. For sample 864, it was observed that away from the Si central reflectivity peaks, the major superlattice peaks began to split into two components. Models containing identical numbers of layers within all the repeated units could not reproduce the experimental curves. Figure 4.34 shows experimental measurements (red) and calculated reflectivity fits for models in which all the identical repeated units contained either 3 (black) or 4 (green) MLs of  $MnF_2$ . A

model which did fit the split reflectivity peaks was found and contained 4 repeated units with 3 ML of  $MnF_2$  and 6 repeated units with 4ML of  $MnF_2$  (an average of 3.6 ML of  $MnF_2$  per repeated unit - shown in blue in figure 4.34).



Figure 4.34: Sample 864, near Si(111) peak, Red - Experimental, Blue - Simulated fit with 3.6  $MnF_2$  layers in repeated unit, Green - 4, Black - 3

Figures 4.35 and 4.36 show the experimental (red) and calculated reflectivity near the Si(111) peak for superlattices containing 36 MnF<sub>2</sub> and 143 CaF<sub>2</sub> layers (blue) and 35 MnF<sub>2</sub> and 143 CaF<sub>2</sub> layers (green) respectively. The model using 36 ML of MnF<sub>2</sub> is observed to accurately fit the experimental values (figure 4.35), whereas in figure 4.36, the calculated and experimental minor superlattice peaks can be seen to be drifting out of phase. This shows that the addition (or removal) of a single MnF<sub>2</sub> layer in the model produces a measurable difference in the reflectivity minor peak separation.

## 4.8 Conclusions

Our results demonstrate that the modified semi-kinematical ROD software can be used to successfully determine the structure of a complex superlattice. The number of arithmetical operations carried out by ROD scales as the first power of the number of atoms contained



Figure 4.35: Experimental reflectivity measurements (red) of sample 863, near to the Si(111) peak and a simulated fit (blue) with the correct number of layers within the superlattice (36 TL of  $MnF_2$  and 143 TL of  $CaF_2$ )



Figure 4.36: Experimental reflectivity measurements (red) of sample 863, near to the Si(111) peak and a simulated fit (green) carried out with a superlattice containing one  $MnF_2$  TL less (35 TL  $MnF_2$ ) than the simulation in figure 4.35

within the simulation (ROD essentially adds the complex-valued scattering factors of all the atoms within the simulation). Provided sufficient computational storage space and numerical precision is available, simulations containing of the order of a hundred thousand atoms (equivalent to several tens of thousands of atomic layers) could be realistically envisaged. The sensitivity and flexibility of the technique have also been discussed. We have determined the 3-D structure of the mature, buried  $CaF_2$ -Si(111) interface using x-ray diffraction reflectivity and CTR scans. We show that samples grown with a high temperature  $CaF_2$  buffer possess, initially a "short" type–B interface that converts on atmospheric exposure to the "long" type–B  $CaF_2$ -Si(111) interface. Our model is consistent with previous models proposed by Lucas [27], Sokolov [36] and Harada [37]. We have observed a fluorite structural phase for the ultrathin MnF<sub>2</sub> layers within the repeated superlattice unit, stabilised by MBE growth, as opposed to its bulk rutile structure.

# Chapter 5

# Growth of Tl on InSb(001)– $c(4 \times 4)$

### 5.1 Introduction

Long-Wavelength Infra-Red (LWIR) (8–12  $\mu$ m  $\equiv$  0.155–0.103 eV) photo-detectors are required for focal plane arrays (FPAs) for use in medical imaging, remote sensing, ecological monitoring and defence. Most LWIR detectors are currently manufactured from HgCdTe alloys. These suffer from a number of metallurgical problems: poor thermal stability; low mechanical strength; and non-uniform composition. There is a considerable research effort to develop alternatives based on the more robust III-V semiconductor alloys. The band gaps of all known III-V binary semiconductor compounds are, however, too large for efficient detection in the LWIR range. Indium antimonide (InSb) has the narrowest band gap (0.18eV at room temperature) of all the III–V zincblende semiconductors and responds to the Mid-Wavelength Infra-Red (MWIR) (3–7  $\mu$ m  $\equiv$  0.414–0.177 eV) band. A highly promising idea is the development of narrow band-gap, ternary and quaternary semiconductors for LWIR photo-detection [54–56].

TISb is a semi-metal with a band gap of -1.6eV that stabilises in the caesium chloride (CsCl) structure. However, a full-potential linear muffin tin orbital calculation predicts that TISb in a zincblende structure can be stabilised [57]. Ab-initio calculations [58] suggest that a compound with LWIR capabilities could be produced by alloying small amounts of Tl (below the calculated solubility limit of x = 0.15) with InSb to produce the ternary semiconductor  $In_{1-x}Tl_xSb$ . This material would be of the desired zinc-blende structure and have a lattice constant only 2% smaller than that of InSb, facilitating epitaxial growth of  $In_{1-x}Tl_xSb$  on InSb. Local density function theory predicts a range of stable phases of  $In_{1-x}Tl_xSb$  [59]. Alloying at x = 0.09,  $In_{1-x}Tl_xSb$  is predicted to have narrower band gap (+0.1 eV) than InSb. In theory, varying the amount of thallium incorporation from x = 0 (InSb) to x = 1 (TlSb) offers the possibility of producing a ternary material with a tunable photo-response in the desired LWIR region from +0.18 eV to -1.6 eV.  $In_{0.91}Tl_{0.09}Sb$  is predicted to have a calculated average bond energy of 1.43 eV, making it more robust for use in FPAs than Hg<sub>0.78</sub>Cd<sub>0.22</sub>Te, which has the same band gap but an average bond energy of only 0.88 eV.

A preliminary experimental study of the incorporation of small amounts (x < 0.05) of Tl into InSb [60] showed that the lattice of the  $In_{1-x}Tl_xSb$  epilayers contracted gradually as more Tl was incorporated. This contradicted earlier atomic size effect calculations [61] and differed from the behaviour of all other group III elements incorporated into III–V materials. This was the motivation for the present study of the in-situ measurement of the growth process.

Using surface x-ray diffraction (SXRD) measurements at Daresbury Laboratory the atomic arrangements of the Sb rich c(4x4) and In rich  $c(8\times2)$  surface reconstructions of InSb(001) [62, 63] have been identified. The results indicated why the  $c(4\times4)$  reconstruction, which exhibits minimal subsurface disruption, is preferred to the  $c(8\times2)$  surface as a starting point for device growth. The  $c(8\times2)$  reconstruction has been recently shown to extend much further (approximately seven atomic layers) into the bulk [64] than the  $c(4\times4)$  reconstruction, forming a larger non-uniformity in the surface region. In addition, the  $c(8\times2)$  surface is characterised by chains of metallic indium. The greater non-uniformity of the surface region and the metallic chains result in the reduced performance of thin InSb film devices.

We present a real-time, in-situ, SXRD (using radiation from a synchrotron source) and Auger electron spectroscopy (AES) study of the optimal cleaning procedure for Sb capped and uncapped InSb wafers, the formation of the InSb(001)-c(4×4) surface reconstruction and the subsequent growth of Tl onto this starting surface, a prerequisite for understanding the preferred formation of thallium and antimony based compounds on the InSb(001) surface.

# 5.2 InSb

### 5.2.1 Bulk InSb

Indium antimonide crystallises in the face centred cubic, zinc-blende structure. Group III antimony atoms occupy the face centred sites and the group V indium atoms occupy the tetrahedral  $T^+$  sites (shown as red and yellow respectively in figure 5.1). The basis vectors which describe the cubic cell are:

$$\mathbf{A}_{1} = a_{0}\mathbf{i}$$
$$\mathbf{A}_{2} = a_{0}\mathbf{j}$$
$$\mathbf{A}_{3} = a_{0}\mathbf{k}, \qquad (5.1)$$

where the lattice constant of InSb (at room temperature) is  $a_0 = 6.47877$  Å.



Figure 5.1: The cubic bulk unit cell of InSb (In - yellow, Sb - red)

#### 5.2.2 InSb(001) surface notation

Figure 5.2 shows a plan view of the InSb(001) surface. The in-plane bulk lattice vectors  $\mathbf{A}_1$  and  $\mathbf{A}_2$  are indicated in black and the in-plane surface lattice vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are indicated in green.

$$\mathbf{a}_{1} = \frac{1}{2}(\mathbf{A}_{1} - \mathbf{A}_{2}) = \frac{a_{0}}{2}(\mathbf{i} - \mathbf{j})$$
  

$$\mathbf{a}_{2} = \frac{1}{2}(\mathbf{A}_{1} + \mathbf{A}_{2}) = \frac{a_{0}}{2}(\mathbf{i} + \mathbf{j})$$
  

$$\mathbf{a}_{3} = \mathbf{A}_{3} = a_{0}\mathbf{k}$$
(5.2)

$$\begin{bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{bmatrix} = \begin{bmatrix} 0.5 & -0.5 & 0.0 \\ 0.5 & 0.5 & 0.0 \\ 0.0 & 0.0 & 1.0 \end{bmatrix} \begin{bmatrix} \mathbf{A}_1 \\ \mathbf{A}_2 \\ \mathbf{A}_3 \end{bmatrix}$$
(5.3)

$$|\mathbf{a}_1| = |\mathbf{a}_2| = \frac{a_0}{\sqrt{2}} = 4.5812\text{\AA}, |\mathbf{a}_3| = a_0 = 6.47877\text{\AA}$$
 (5.4)

The corresponding reciprocal lattice vectors are:

$$\mathbf{b}_{1} = \frac{2\pi}{a_{0}}(\mathbf{i} - \mathbf{j})$$

$$\mathbf{b}_{2} = \frac{2\pi}{a_{0}}(\mathbf{i} + \mathbf{j})$$

$$\mathbf{b}_{3} = \frac{2\pi}{a_{0}}\mathbf{k}$$
(5.5)

$$|\mathbf{b}_1| = |\mathbf{b}_2| = \frac{2\pi}{a_0}\sqrt{2} = 1.37152\text{\AA}^{-1}, |\mathbf{b}_3| = \frac{2\pi}{a_0} = 0.96981\text{\AA}^{-1}.$$
 (5.6)

Following the method described in section 4.2.2 on page 65, the transformation between surface and bulk co-ordinate systems is:

$$x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3 = X\mathbf{A}_1 + Y\mathbf{A}_2 + Z\mathbf{A}_3, \tag{5.7}$$

$$\begin{bmatrix} x & y & z \end{bmatrix} \begin{bmatrix} 0.5 & -0.5 & 0.0 \\ 0.5 & 0.5 & 0.0 \\ 0.0 & 0.0 & 1.0 \end{bmatrix} = \begin{bmatrix} X & Y & Z \end{bmatrix}$$
(5.8)

where lower and upper case letters indicate surface and bulk systems respectively.



Figure 5.2: A plan view of the InSb(001) surface showing bulk indium (yellow) and antimony atoms (red). The bulk and surface unit cells are shown in black and green respectively

#### 5.2.3 InSb(001)-c( $4 \times 4$ )

A variety of reconstructions of the InSb(001) surface have been identified and measured using a wide range of electronic and photonic probes including: STM; LEED; RHEED; HEED; synchrotron core level photoemission spectroscopy; and surface x-ray diffraction. The most ordered reconstructions are the Sb rich  $c(4\times4)$  [62, 65, 66] and the In rich  $c(8\times2)$  [64, 67].

The accepted structure for the  $c(4\times4)$  reconstruction is the missing dimer model, proposed by John [65] to fit core level photoemission and HEED measurements. Subsequent structural and compositional analyses carried out by McConville [66] (using STM) and by Jones [62] (using SXRD) refined the model. In the model, 3/4 of a monolayer of Sb is absorbed onto a fully Sb terminated InSb bulk (In and Sb atoms are shown as yellow and red respectively in figure 5.3). The upper Sb layer consists of repeated units, each containing three sets of Sb dimers (shown in blue in figure 5.3) followed by a dimer vacancy. The Sb–Sb dimer bonds and the length of the three dimer repeat lie parallel to the [110] and the [110] directions respectively. The primitive  $p(4\times4)$  and centred  $c(4\times4)$ surface cells are shown in figure 5.3 in red and blue respectively.

The surface lattice vectors,  $\mathbf{a}_i^*$ , defining the  $c(4 \times 4)$  unit cell are:

$$\mathbf{a}_{1}^{\star} = 2\mathbf{a}_{1} + 2\mathbf{a}_{2} = 2a_{0}\mathbf{i}$$
$$\mathbf{a}_{2}^{\star} = -2\mathbf{a}_{1} + 2\mathbf{a}_{2} = 2a_{0}\mathbf{j}$$
$$\mathbf{a}_{3}^{\star} = \mathbf{a}_{3} = a_{0}\mathbf{k}$$
(5.9)

$$\begin{bmatrix} \mathbf{a}_{1}^{\star} \\ \mathbf{a}_{2}^{\star} \\ \mathbf{a}_{3}^{\star} \end{bmatrix} = \begin{bmatrix} 2.0 & 0.0 & 0.0 \\ 0.0 & 2.0 & 0.0 \\ 0.0 & 0.0 & 1.0 \end{bmatrix} \begin{bmatrix} \mathbf{A}_{1} \\ \mathbf{A}_{2} \\ \mathbf{A}_{3} \end{bmatrix}$$
(5.10)

$$|\mathbf{a}_{1}^{\star}| = |\mathbf{a}_{2}^{\star}| = 2a_{0} = 12.95754\text{\AA}, |\mathbf{a}_{3}^{\star}| = a_{0} = 6.47877\text{\AA}$$
 (5.11)



**Figure 5.3:** The InSb(001)-c(4×4) surface cell showing bulk indium (yellow) and antimony (red) atoms and antimony surface dimers (blue). The  $p(4\times4)$  and  $c(4\times4)$  surface cells are indicated in red and blue respectively

The corresponding reciprocal  $c(4 \times 4)$  surface lattice vectors are:

$$\mathbf{b}_{1}^{\star} = \frac{\pi}{a_{0}}\mathbf{i}$$
$$\mathbf{b}_{2}^{\star} = \frac{\pi}{a_{0}}\mathbf{j}$$
$$\mathbf{b}_{3}^{\star} = \frac{2\pi}{a_{0}}\mathbf{k}$$
(5.12)

$$\mathbf{b}_{1}^{\star} \mid = \mid \mathbf{b}_{2}^{\star} \mid = \frac{2\pi}{a_{0}}\sqrt{2} = 0.48491 \text{\AA}^{-1}, \mid \mathbf{b}_{3}^{\star} \mid = \frac{2\pi}{a_{0}} = 0.96981 \text{\AA}^{-1}.$$
(5.13)

The reciprocal-space reflections for the  $c(4\times4)$  surface, in terms of the  $(1\times1)$  unit reciprocal vectors,  $\mathbf{b}_i$ , and the  $c(4\times4)$  reciprocal vectors,  $\mathbf{b}_i^*$  are illustrated in figure 5.4.



**Figure 5.4:** The reciprocal space reflections for the  $InSb(001)-c(4\times 4)$ reconstruction in terms of the  $(1\times 1)$  reciprocal unit vectors,  $\mathbf{b}_i$ , and the  $c(4\times 4)$ reciprocal vectors,  $\mathbf{b}_i$ 

# 5.3 Experimental

The major objectives of the experiment were:

- to determine the optimum cleaning and decapping conditions to produce atomically clean, well ordered, InSb(001)-c(4×4) surface reconstructions using SXRD and AES;
- to monitor the growth of thallium on InSb(001)-c(4×4) and determine the growth mode and morphology of the developing layer. This was achieved by measuring the specular intensity and the diffuse tail close to the anti-phase position between the Bragg peaks of InSb as a function of Tl deposition time;
- and on completion of the growth, to determine the structure and chemical composition of the thallium layers using in-plane and full specular reflectivity x-ray diffraction scans and AES.

The III-V semiconductor research group at QinetiQ (formerly the Defence Evaluation and Research Agency (DERA)), Malvern, are highly experienced in the growth of InSb and other Sb based semiconductors. The InSb substrates provided by them for this experiment have the same high levels of purity, structural order and surface miscut as those used for device production.

Circular (three inch diameter), n-type, InSb(001) wafers (Wafertech) were loaded into the InSb dedicated MBE chamber at QinetiQ and annealed at 250°C for 24 hours. The thermocouple was calibrated by measuring the temperature at which InSb and GaSb surface reconstruction phase transitions occurred. Prior to growth, the wafer was held under an antimony over-pressure and the substrate temperature,  $T_s$ , increased until the surface contaminants started to desorb ( $\approx$ 400°C) and a c(4×4) reconstruction was observed using RHEED. The substrate was stabilised at this temperature, and annealed for twenty minutes to fully remove the surface impurities. The sample was then cooled to the growth temperature ( $T_s = T_t + 35°C$ , where  $T_t$  ( $\approx$  300°C) is the static transition temperature from the (1×1) to the c(4×4) surface reconstruction) and a 1µm thick, high quality crystalline, undoped InSb buffer layer grown under excess Sb conditions. Optionally, an undoped 1000Å thick Sb protective cap was grown at  $T_s = 250^{\circ}C$ .

Sb capped and uncapped samples were transported to Leicester and stored under low vacuum.  $8 \times 8$ mm cleaved sections of the InSb wafers were bonded to thoroughly outgassed  $10 \times 8$ mm molybdenum backing plates using a small amount of molten indium. The samples were then mounted on a sample holder and transferred via the sample transfer port into the SXRD UHV chamber.

The LUXC chamber was coupled (via a differentially pumped rotary seal) to the 6-circle diffractometer at station 9.4 of the SRS at Daresbury. The x-ray measurements were made using x-rays with a wavelength of 0.9Å (energy = 13.788 keV) and detected using a liquid nitrogen cooled, solid state germanium detector. The end of beam, pre-sample, slits were set to define the incident x-ray beam to be 2mm (horizontally) × 1mm (vertically). The post sample slits (which define the active area on the sample surface observed by the detector) and the detector slits (which define the *l* resolution of the diffracted beam) were set to 10mm (horizontally) × 2mm (vertically) and 3mm (horizontally) × 10mm (vertically) respectively.

A comprehensive account of the LUXC UHV chamber, the 6-circle diffractometer at station 9.4, and the procedure used to mount the cleaved wafer sections is given in section 3.3.
# 5.4 Results

#### 5.4.1 Sb capped InSb(001) samples

#### AES measurements of the "as-loaded" capped sample before and after cleaning

After loading an antimony capped InSb(001) sample into the SXRD chamber, an initial AES scan, shown in black in figure 5.5, shows the sample surface to be heavily contaminated by carbon and oxygen (Sb : C : O ratio = 1 : 0.8 : 0.4). A number of methods are available to remove surface contaminants from InSb (001) substrates [68]: thermal desorption; Ar<sup>+</sup> ion bombardment followed by annealing; Ar<sup>+</sup> ion bombardment at elevated substrate temperatures; irradiation with atomic hydrogen; and exposure to an electron cyclotron resonance (ECR) hydrogen plasma. Of the methods available to us, Ar<sup>+</sup> ion bombardment at elevated substrate temperatures produced the best results.



Figure 5.5: AES measurements of an Sb capped InSb sample before cleaning (black) and after  $Ar^+$  bombardment (red), showing the removal of oxygen and carbon based contaminants

Prior to removal of the Sb capping layer, the sample was heated to approximately 200°C

(below the Sb evaporation temperature). At this elevated temperature, a thirty minute bombardment cycle of 900eV Ar<sup>+</sup> ions (2–3  $\mu$ A beam current) was sufficient to remove all traces of oxygen and carbon based surface contamination, leaving a clean antimony auger signal produced by the capping layer (shown in red in figure 5.5). The cleanliness of the Ar gas was monitored throughout the sputtering phase using a mass spectrometer to ensure an Ar (40 a.m.u) : N<sub>2</sub> / CO (28 a.m.u) ratio of at least 100 : 1.

The diffractometer  $\chi$  arc and  $\phi$  circle (see figure 3.5) were optimised to minimise the precession of a laser beam reflected from the sample surface as the  $\omega$  circle, on which the  $\chi$  arc and  $\phi$  circle are mounted, was rotated. In this manner, the surface normal of the sample was aligned with the diffractometer to within 0.03°. A full description of the diffractometer alignment procedure is given in section 3.6. The sample was crystallographically aligned by measuring two InSb Bragg x-ray reflections, allowing the calculation of the "UB" matrix, a co-ordinate transformation from the diffractometer frame of reference to the sample's reciprocal-space frame of reference.

In-plane measurements were performed with an incident angle of either 0.8° or 1.7° (corresponding to l = 0.1 or 0.2), well above the critical angle,  $\theta_c$ , for InSb ( $\theta_c = 0.19^\circ$  at an x-ray wavelength of 0.9Å). At the critical angle, small changes in the incident angle can produce large variations in the reflected and refracted intensities. At larger incident angles ( $\approx 4\theta_c$  and  $8\theta_c$ ), the reflective and refractive intensity are approximately constant for small perturbations in the incident angle.

#### X-ray measurements before the decapping procedure

Prior to decapping the protective antimony layer, in-plane x-ray scans were performed to search for evidence of a buried surface reconstruction or diffraction peaks produced by the antimony capping layer. Figures 5.6 and 5.7 show in-plane scans along the  $\mathbf{b}_1$  axis (measured in terms of h) and the  $\mathbf{b}_2$  axis (measured in terms of k) respectively. Both in-plane scans show a weak reflection at h or k = 1.22 and a much stronger reflection (overloading the detector without beam attenuation) at h or k = 1.47. The equal strengths of each type of peak in the  $\mathbf{b}_1$  and  $\mathbf{b}_2$  in-plane directions indicates that there is no preferred orientation axis for the amorphous Sb layers.



**Figure 5.6:** In-plane  $(h \ 0 \ 0.1)$  x-ray scan along the  $\mathbf{b}_1$  direction of an Sb capped InSb sample, showing antimony peaks at  $h = \pm 1.22$  and  $\pm 1.47$ , prior to decapping

#### The structure of antimony

To index the antimony peaks shown in figures 5.6 and 5.7, a full understanding of the crystal structure of bulk antimony is required. Antimony crystallises in the trigonal,  $\alpha$ As (A7) structure (space group number 166). The hexagonal unit cell is shown in figure 5.8. The interlayer spacings,  $d_{HKL}$ , for an hexagonal unit cell can be calculated using:

$$d_{HKL} = \frac{1}{\sqrt{\frac{4}{3a^2}(H^2 + HK + K^2) + \frac{L^2}{c^2}}},$$
(5.14)

where a = 4.307Å and c = 11.273Å for antimony. The reflection produced by a lattice spacing of  $d_{HKL}$ , can then be converted to the tetragonal scattering vectors of InSb



Figure 5.7: In-plane  $(0 - k \ 0.1)$  x-ray scan along the  $\mathbf{b}_2$  direction of an Sb capped InSb sample, showing antimony peaks at k = -1.22 and -1.47. The symmetry of the peaks in the  $\mathbf{b}_1$  and  $\mathbf{b}_2$  directions proves the amorphous nature of the capping layer

(measured in terms of h, k and l):

$$h = \frac{\sqrt{\frac{4\pi^2}{d_{HKL}^2} - k^2 |\mathbf{b}_2|^2 - l^2 |\mathbf{b}_3|^2}}{|\mathbf{b}_1|}$$
(5.15)

Only hexagonal reflections which satisfy the criterion -H + K + L = 3N, where N is an integer, are allowed. The relative intensities of the allowed reflections can be calculated using inorganic crystal structure database (ICSD) software from the online chemical database service (CDS) at Daresbury<sup>1</sup>. The strongest reflection is defined to have an intensity of 1000, all other intensities are quoted relative to this value. Table 5.1 summarises the allowed reflections for antimony and gives the relative intensity and corresponding h value for each reflection. Analysis of table 5.1 shows that the weak and strong diffraction peak at h = 1.22 and 1.47 are produced by the hexagonal (0 0 3) and

<sup>&</sup>lt;sup>1</sup>http://cds3.dl.ac.uk/cgi-bin/icsd/icsd.cgi

# 11.273 Å

During the store, tow beapars in this among yeak intens 165°C. As the shapple to spe

4.307 Å Figure 5.8: The hexagonal unit cell of bulk antimony

	H	K	L	-H + K + L	$d_{HKL}$	Intensity	$h \ (k = 0,  l = 0.1)$
	0	0	3	3	3.758Å	27.6	1.217
i	1	0	1	0	3.542Å	8.1	1.291
ņ	0	1	2		3.111Å	1000	1.471
	1	0	4	3	2.249Å	387	2.036
E	1	1	0		2.154Å	375	2.126

 Table 5.1: The relative strength and reciprocal-space location of antimony

 powder diffraction peaks

4.307 Å

#### X-ray measurements during the decapping process

The x-ray detector and diffractometer were positioned to monitor the  $(1.47 \ 0 \ 0.1)$ antimony peak during the thermal desorption of the antimony capping layer. Desorption was carried out under an antimony over-pressure (the Sb Knudsen cell evaporator was heated to 430–460°C, producing a vapour pressure of  $10^{-5}$ – $10^{-4}$  Torr) to maintain the In : Sb surface stoichiometry, ensuring the surface did not become irreversibly In rich. Two methods were used to decap the sample: a slow, low temperature anneal; and a rapid, high temperature anneal.

During the slow, low temperature anneal, shown in figure 5.9, a sudden dramatic reduction in the antimony peak intensity was observed at a sample temperature of approximately 165°C. As the sample temperature was increased, the intensity rose again to it's previous value and levelled off at around 210°C. Subsequent x-ray measurement showed the sample was still crystallographically aligned, ruling out any movement of the sample on the molybdenum backing plate as the indium seal became molten (the melting point of indium is 157°C) and proving that a substantial re-ordering of the capping layer had occurred. After the low temperature anneal, the sample was allowed to cool to room temperature. The antimony peak after the re-ordering process was found to be approximately one and a half times more intense than before the low temperature anneal.

The rapid, high temperature anneal is shown in figure 5.10. Above 250°C a gradual depletion of antimony was observed. At approximately  $305^{\circ}$ C a more dramatic antimony loss was measured. The sample was cooled slightly to achieve a dynamical equilibrium between the incident flux of antimony and thermal desorption of antimony from the sample surface. In this temperature regime, the antimony atoms have sufficient thermal energy to move freely over the sample surface and to form the  $c(4\times4)$  reconstruction, a local minimum in the surface energy.



Figure 5.9: Monitoring the (1.47 0 0.1) amorphous antimony diffraction peak during a low temperature sample anneal, showing a re-ordering of the protective Sb capping layer at around 180°C



**Figure 5.10:** Monitoring the (1.47 0 0.1) amorphous antimony diffraction peak during a high temperature sample anneal, showing the depletion and subsequent removal of the protective Sb capping layer

#### AES measurements after the decapping process

An AES scan performed immediately after the decapping procedure showed a clean (no oxygen or carbon contamination) surface (see figure 5.11) with a peak-to-peak Sb:In ratio of approximately 1.2, indicative of the formation of the Sb-rich  $c(4\times4)$  reconstruction. The lack of contamination proved that the Sb capping layer was of sufficient thickness to protect the InSb buffer layer during 12 months of atmospheric exposure. In addition, no sample contamination from the heater filament or the sample holder was observed during the high temperature decapping procedure.



**Figure 5.11:** AES after the decapping procedure showing no indication of C or O contamination and an Sb : In ratio of 1.2, indicative of the formation of the Sb-rich  $c(4 \times 4)$  reconstruction

#### The formation of the $c(4 \times 4)$ reconstruction

After the decapping procedure, the sample was held under an Sb over-pressure and annealed whilst monitoring the intensity of the  $(0.5 \ 0 \ 0.2) \ c(4 \times 4)$  reconstruction peak

(see figure 5.12). At 180°C a sudden increase in the peak height was observed, the maximum intensity was attained by stabilising the sample at 250°C.



Figure 5.12: Annealing the sample under an antimony over-pressure after decapping whilst monitoring the  $(0.5 \ 0 \ 0.2) \ c(4 \times 4)$  reconstruction peak

In-plane scans along the  $\mathbf{b}_1$  and  $\mathbf{b}_2$  directions (figures 5.13 and 5.14) show a well ordered  $c(4\times 4)$  reconstruction. An extra Sb peak was measured in the  $\mathbf{b}_2$  direction at k = 1.21 (figure 5.14). This feature can be attributed to the (0 0 3) hexagonal planes of bulk antimony. Verification that the extra peak was a real feature of the sample surface (rather than scattering from the tantalum clips or molybdenum backing plate), was obtained by measuring an identical peak at k = -1.22. The Sb peak indicates regions of the sample surface are still partly covered by Sb. The absence of a similar peak in the  $\mathbf{b}_1$  direction.



**Figure 5.13:** In-plane  $(h \ 0 \ 0.1)$  x-ray scan along the  $\mathbf{b}_1$  direction showing a well formed InSb(001)-c(4×4) surface reconstruction



Figure 5.14: In-plane (0 k 0.1) x-ray scan along the  $\mathbf{b}_2$  direction showing a well formed InSb(001)-c(4×4) surface reconstruction and extra peak at k = 1.21

#### 5.4.2 Uncapped InSb(001) samples

AES measurements of the "as-loaded" uncapped sample before and after cleaning

Having determined the optimum decapping and cleaning conditions for antimony capped wafers, a similar procedure was developed for uncapped wafers. An initial AES scan of the as-loaded wafer showed heavy carbon based surface contamination (the black curve in figure 5.15) (Sb : C : O ratio = 1 : 1.7 : 0.85). A thirty minute Ar<sup>+</sup> ion bombardment (with the same settings used in the capped wafer sputtering procedure described in section 5.4.1) at elevated temperature (approximately 250°C) and under an Sb over-pressure was sufficient to remove the surface contamination (the red curve in figure 5.15). The elevated temperature allowed the re-ordering of the sample surface and the desorption of embedded Ar<sup>+</sup> ions.



Figure 5.15: AES measurements of an uncapped InSb sample before cleaning (black) and after  $Ar^+$  bombardment (red)

#### X-ray measurements during the cleaning procedure

After  $Ar^+$  ion bombardment, a weak  $c(4 \times 4)$  reconstruction was observed using in-plane scans (shown in red in figure 5.17). The intensity of the (0.5, 0, 0.2) c(4×4) reconstruction diffraction peak was monitored as the sample was annealed under an antimony flux (figure 5.16). At approximately 180°C an ordering in the surface reconstruction was observed. During the decapping of Sb capped samples (described in section 5.4.1), an ordering of the Sb capping layer was also observed at 170°C, indicating the increased mobility of Sb atoms at this temperature. Above  $300^{\circ}$ C the intensity of the (0.5, 0, 0.2) peak decreased, indicating a preferential loss of antimony from the surface. Jones [68] showed that between 310°C and 360°C the InSb(001) surface undergoes a continuous structural transition from the  $c(4\times 4)$  to the asymmetric  $(3\times 1)$  reconstruction. In our experiment, the  $c(4\times 4)$ reconstruction was reformed by cooling the sample to approximately 270°C, establishing the reversibility of the structural transition. On cooling the sample to room temperature, the  $c(4 \times 4)$  reconstruction weakened. A second annealing cycle at 270°C, under an Sb over-pressure, was required to stabilise the intensity of the reconstruction peak at room temperature. Figure 5.17 shows in-plane scans at key stages during the cleaning and reconstruction formation procedure. Verification of the  $c(4 \times 4)$  reconstruction was provided by observing similar diffraction peaks at k = 0.5, 1.0 and 1.5 in the  $\mathbf{b}_2$  direction (figure 5.18).

### 5.4.3 The growth of Tl on $InSb(001)-c(4\times 4)$

The earliest attempts to grow  $In_{1-x}Tl_xSb$  using MBE were carried out by Wood [69]. Using secondary ion mass spectrometry (SIMS) they estimated an optimum thallium incorporation of 5% at a substrate temperature of 300°C. The surface stoichiometry was consistent with either thallium atoms occupying the indium sublattice positions, or precipitation of a second phase material on the sample surface. No increase in the absorption cutoff wavelength was detected.



Figure 5.16: Annealing the sample under an antimony over-pressure whilst monitoring the formation of the  $(0.5 \ 0 \ 0.2) \ c(4 \times 4)$  reconstruction peak



**Figure 5.17:** An in-plane  $(h \ 0 \ 0.1)$  x-ray scan along the  $\mathbf{b}_1$  direction during the formation of the  $c(4 \times 4)$  reconstruction



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**Figure 5.18:** An in-plane  $(0 \ k \ 0.1)$  x-ray scan along the  $\mathbf{b}_2$  direction showing the  $\mathbf{c}(4 \times 4)$  reconstruction

Growth of  $In_{1-x}Tl_xSb$  and InSb on GaAs substrate by low-pressure metal-organic chemical vapour deposition (LP-MOCVD) was reported by Choi [70]. An unspecified amount of Tl was incorporated, but in contrast to Wood, the optical properties of the ternary alloy showed an absorption shift at 77K from 5.5 $\mu$ m for InSb to 8 $\mu$ m for InTlSb. This was also confirmed by photoconductivity measurements. X-ray measurements showed shoulders to the InSb(004) and (008) peaks, indicative of a  $In_{1-x}Tl_xSb$  film with a similar lattice constant to InSb.

Karam [71] reported a thallium incorporation of up to x=0.1 in  $In_{1-x}Tl_xSb$  layers grown on GaAs and InSb substrates using MOCVD. Rutherford backscattering and room temperature infra-red transmission spectra showed considerable absorption of the material beyond  $7\mu$ m and into the LWIR range. Spectral response measurements showed substantial photoresponse at  $8.5-14\mu$ m.

Electron microprobe analysis (EMPA) by Huang [72], showed less than 1% Tl incorporation in InSb during high temperature (400–475°C) MOCVD growth. Only the formation of InSb, metallic Sb and liquid In + Tl + Sb was detected. They suggest

that the theoretical solubility of 15% Tl in InSb is unrealistically high due to the use of an artificially high value for the melting temperature of TlSb in the thermodynamic calculations. They estimate the solubility to be less than 2%.

Lee [60] measured the infrared photoresponse spectra of  $In_{1-x}Tl_xSb$  LP-MOCVD epilayers and detected a clear shift to longer wavelengths than InSb. Contrary to theory, high resolution x-ray diffraction measurements showed that  $In_{1-x}Tl_xSb$  epilayers contracted as more Tl was incorporated. This behaviour differs from other group III impurities in III antimonides. The low oxidation state of Tl in  $In_{1-x}Tl_xSb$  was suggested as a possible reason for the observed lattice contraction. Considerable oxygen and carbon based contamination of the layer was revealed using AES.

Investigation of gas source MBE growth of  $In_{1-x}Tl_xSb$  was reported by Antonell [73]. Growth of Tl-Sb binaries produced  $Tl_7Sb_2$  and Sb, with no elemental Tl. Above 350°C the sticking co-efficient of Tl decreases rapidly with increasing temperature. At 425°C total desorption of Tl results. Attempts to grow ternary  $In_{1-x}Tl_xSb$  resulted in a three-phase mixture of  $Tl_7Sb_2$ , InSb and metallic Sb. A shell of the  $Tl_7Sb_2$  phase formed around Sb droplets. They observed group V metallic Sb rather than elemental Tl, in contrast to the behaviour of InTlAs. They speculate that in the experiments carried out by Wood [69] the apparent concentration of Tl may be a consequence of Tl-Sb liquid accumulation on the surface during growth that solidifies on cooling.  $Tl_7Sb_2$  readily oxidised.

Using reflectance and x-ray diffraction no Tl incorporation was detected by Ruiz-Becerril [74] for  $In_{1-x}Tl_xSb$  layers grown by liquid phase epitaxy (LPE).

Razeghi [75] reports  $In_{1-x}Tl_xSb$  alloys grown on GaAs substrates with various Tl compositions grown using LP-MOCVD and characterised using x-ray diffraction, Hall measurements, infrared transmission and photoconductivity measurements. The photoresponse cut-off was tailored from 5.5–9  $\mu$ m, with a -1.3% lattice mismatch. The bandgap was further decreased by higher Tl incorporation.

Further experimentation is required to resolve the debate about the maximum

incorporation of Tl into a InSb matrix. A prerequisite for the growth of  $In_{1-x}Tl_xSb$ on the InSb(001)-c(4×4) surface reconstruction is the growth of Tl on InSb to understand the atomic interactions between Tl and Sb and the preferred formation of Tl-Sb based compounds. After forming a well ordered InSb(001)-c(4×4) reconstruction, the objective was to deposit Tl and characterise the growth mode and structure of the Tl and Sb based compounds formed. Thallium crystallises in the "A3" hexagonal close pack structure (HCP) (space group number 194). The hexagonal unit cell is show in figure 5.19.



Figure 5.19: The hexagonal unit cell of bulk thallium

#### **Experimental** methods

The detector and the diffractometer were positioned at the InSb anti-phase position, h = k = 0 and l = 1, prior to the growth of thallium (the first InSb Bragg peak is at l = 2). Maintaining the sample at room temperature, the thallium Knudsen cell was heated to approx 380°C, producing a vapour pressure of  $10^{-6}$  Torr. After measuring a background level at the anti-phase position, the evaporator shutter was opened and the change in the peak intensity monitored as a function of time during deposition of thallium (see figure 5.20).



Figure 5.20: Experimental measurements of the intensity of the InSb (0, 0, 1) anti-phase position during deposition of thallium onto the InSb(001)-c $(4\times4)$  reconstruction (red). A calculated layer-by-layer growth model with no thallium incorporated into the top Sb layer is shown in blue. A calculated layer-by-layer growth model incorporating up to 0.25 ML of thallium in the top Sb layer (which contain 0.75 ML Sb) is also shown in black. The Tl interplanar separation was set to its bulk value of 2.7625Å

#### Fitting the Tl on InSb-c( $4 \times 4$ ) growth curves

The structure factor for the InSb bulk, the  $c(4\times4)$  reconstruction and the deposited layers of Tl (as a function of coverage) can be calculated individually and combined with appropriate phase factors to produce an expression for the total structure factor as a function of l. The structure factor for the InSb bulk unit cell is:

$$F_{\text{unit}}(l) = 2f_{\text{Sb}} + 2f_{\text{Sb}}e^{-\pi i l} + 2f_{\text{In}}e^{-\frac{\pi i l}{2}} + 2f_{\text{In}}e^{-\frac{3\pi i l}{2}}$$
  
$$= 2e^{-\pi i l} \left\{ f_{\text{Sb}}e^{-\frac{\pi i l}{2}} \left( e^{\frac{\pi i l}{2}} + e^{\frac{\pi i l}{2}} \right) + f_{\text{In}} \left( e^{\frac{\pi i l}{2}} + e^{\frac{\pi i l}{2}} \right) \right\}$$
  
$$= 4e^{-\pi i l} \cos \left( \frac{\pi l}{2} \right) \left\{ f_{\text{Sb}}e^{\frac{\pi i l}{2}} + f_{\text{In}} \right\}$$
(5.16)

The structure factor for the entire InSb bulk, neglecting the attenuation of the beam as it passes through the bulk, can be calculated by performing a semi-infinite sum of the contributions from all the individual unit cells:

$$F_{\text{bulk}}(l) = F_{\text{unit}}(l) \left(1 + e^{2\pi i l(-1)} + e^{2\pi i l(-2)} + \dots\right)$$
  
=  $F_{\text{unit}}(l) \sum_{n=0}^{\infty} e^{-2\pi i l n}$   
=  $\frac{F_{\text{unit}}(l)}{1 - e^{-2\pi i l}}$  (5.17)

Substituting the expression for the unit cell structure factor (equation 5.16) into equation 5.17 leads to:

$$F_{\text{bulk}}(l) = \frac{4e^{-\pi i l} \cos\left(\frac{\pi l}{2}\right) \left\{ f_{\text{Sb}} e^{\frac{\pi i l}{2}} + f_{\text{In}} \right\}}{1 - e^{-2\pi i l}} \\ = \frac{-2i \cos\left(\frac{\pi l}{2}\right) \left\{ f_{\text{Sb}} e^{\frac{\pi i l}{2}} + f_{\text{In}} \right\}}{\sin\left(\pi l\right)}$$
(5.18)

The  $c(4\times4)$  reconstruction is produced by adding an extra three quarters of a monolayer of antimony onto the Sb-terminated InSb bulk. The structure factor for the extra 3/4ML of Sb is:

$$F_{\rm recon}(l) = \frac{3}{4} \times 2f_{\rm Sb}e^{\frac{\pi i l}{2}} = \frac{3}{2}f_{\rm Sb}e^{\frac{\pi i l}{2}}$$
(5.19)

The total structure factor for the bulk and the reconstruction is:

$$F_{\text{sample}}(l) = F_{\text{bulk}}(l) + F_{\text{recon}}(l) = \frac{-2i\cos\left(\frac{\pi l}{2}\right) \left\{ f_{\text{Sb}} e^{\frac{\pi i l}{2}} + f_{\text{In}} \right\}}{\sin(\pi l)} + \frac{3}{2} f_{\text{Sb}} e^{\frac{\pi i l}{2}}$$
(5.20)

The total structure factor during the growth of Tl on the  $InSb(001)-c(4\times 4)$  reconstruction is:

$$F_{\text{growth}}(l) = F_{\text{sample}}(l) + \alpha f_{\text{Tl}} e^{\frac{\pi i l}{2}} \sum_{n=0}^{\infty} \theta_n e^{\frac{2\pi i l n c}{a}}$$
(5.21)

where  $\alpha$  is required to match the layer densities of InSb and Tl,  $\theta_n$  is the coverage of the *n*th layer of Tl and *c* is the Tl interlayer spacing. InSb has a unit cell area of 6.47877 × 6.47877 Å<sup>2</sup> and Tl has a unit cell area of 3.457 × 3.457 Å<sup>2</sup>. To match the lattice areas,  $\alpha = 3.512$ . The total intensity, *I*, is proportional to the square modulus of the total structure factor:

$$I_{\text{total}}(l) \propto |F_{\text{growth}}(l)|^2$$
 (5.22)

At the InSb anti-phase position (l = 1) the total scattered intensity reduces to:

$$I_{\text{total}}(l=1) \propto \left| \left( 1 + \frac{3}{2}i \right) f_{\text{Sb}} - i f_{\text{In}} + i \alpha f_{\text{Tl}} \sum_{n=0}^{\infty} \theta_n e^{\frac{2\pi i n c}{a}} \right|^2$$
(5.23)

To fit the experimental growth curve, an expression for the relative coverage of each layer of thallium  $\theta_n$ , as a function of deposition time, needs to be calculated. Two simple models were considered:

- Layer-by-layer growth with the first thallium layer separated by a distance c from the top 3/4 ML of Sb (shown in blue in figure 5.20)
- The growth of 1/4 ML of thallium incorporated into the top 3/4 ML of Sb before layer-by-layer growth (shown in black in figure 5.20)

Identical deposition rates, matched to the experimental completion rate of 1 ML in approximately 40 minutes, were used for both growth models. The spacing between the top Sb layer and the first Tl layer and the Tl interplanar spacing were fixed to be the bulk thallium interplanar spacing c = 2.7625Å =  $0.426 \times a_{\text{InSb}}$ .

A calculation (shown in blue in figure 5.20) in which the thallium atoms initially form a new layer a distance c above the top, partially filled (0.75 ML) Sb layer fits the initial

decrease in the experimentally measured intensity. In contrast, the black calculated curve in figure 5.20 modelling the completion of the top partially occupied Sb layer before the formation of a new Tl layer produces an initial increase in intensity. The lack of well formed oscillations in the growth curve after the formation of the first thallium layer is indicative of completion of a wetting layer followed by disordered 3-D island growth (Stranski-Krastanow (SK) mode) rather than well ordered layer-by-layer Frank-van der Merwe (FM) growth.

#### AES after Tl deposition

After two growth cycles (during which approximately 5ML of Tl were deposited) the cleanliness and surface stoichiometry were measured using AES (see figure 5.21). Intense, low energy thallium peaks (54, 84 and 101 eV) and an antimony rich Sb : In ratio were measured. No carbon or oxygen based surface contaminants were detected. In and Sb AES peaks show that even after the growth of approximately 5ML of Tl on the InSb surface, regions of the InSb surface were still uncovered. This confirms the x-ray measurements that the growth mode is disordered 3-D island growth.

#### X-ray measurements of the Tl covered InSb-c( $4 \times 4$ ) surface

After Tl deposition, in-plane  $(h \ 0 \ 0.1)$  and  $(0 \ k \ 0.1)$  scans along the  $\mathbf{b}_1$  and  $\mathbf{b}_2$  directions showed the suppression of the InSb-c(4×4) peaks and the emergence of features at h =1.66 (figure 5.22) and k = 1.634 and 1.721 (figure 5.23).

A number of extra out-of-plane peaks were also observed in a specular reflectivity ridge scan (figure 5.24) in addition to the expected (0 0 2) InSb Bragg reflection at  $\alpha = 15.97^{\circ}$ .

The same method used to calculate the Sb peaks in section 5.4.1 can be used to calculate the relative intensity and location of Tl peaks in the in-plane directions and the out-of-



Figure 5.21: AES scan after the second deposition of Tl onto  $InSb(001)-c(4\times 4)$ , showing intense, low-energy Tl peaks and a Sb rich, Sb : In ratio



**Figure 5.22:** In-plane  $(h \ 0 \ 0.2)$  x-ray scan along the  $\mathbf{b}_1$  direction, showing the formation of a peak at h = 1.66 during the deposition of Tl



**Figure 5.23:** In-plane (0 k 0.2) x-ray scan along the  $\mathbf{b}_2$  direction, showing the formation of peaks at k = 1.634 and 1.721 during the deposition of Tl



Figure 5.24: Specular reflectivity ridge scan after Tl deposition, showing the InSb Bragg reflection at  $\alpha = 15.97^{\circ}$ , extra peaks at  $17.04^{\circ}$ ,  $18.68^{\circ}$  and  $19.41^{\circ}$  produced by Tl and a peak at  $18.17^{\circ}$  produced by Tl<sub>2</sub>O. The peaks at  $21.92^{\circ}$  and  $22.30^{\circ}$  remain unaccounted for

plane direction. For the HCP structure, reflections where L is odd and H + 2K = 3N(where N is an integer) are forbidden, e.g the HCP (1 1 1), (0 0 1), (2 1 1) and (0 0 3) reflections are forbidden. Table 5.2 summarises the allowed reflections for thallium and gives the relative intensity and corresponding h or k value for each reflection.

H	K		$d_{HKL}$	Intensity	$h \text{ or } k \ (l = 0.1)$
1	0	0	2.994Å	229.8	1.524
0	0	2	2.762Å	250.7	1.652
1	0	1	2.632Å	1000	1.735
1	0	2	2.030Å	168.3	2.252
1	1	0	1.728Å	214.2	2.647

**Table 5.2:** The relative strength and reciprocal-space location of thallium powder

 diffraction peaks

Analysis of table 5.2 and the in-plane scans shown in figures 5.23 and 5.24 shows that the extra in-plane peaks at h = 1.66 and k = 1.634 are produced by the (0 0 2) hexagonal planes of Tl. The more intense extra peak at k = 1.721 (approximately twice as intense as the k = 1.634) is produced by the (1 0 1) hexagonal planes of Tl. A lack of the (1 0 1) Tl peak in the h direction shows a preferential alignment of the Tl domains. For the reflectivity ridge scan, the peaks at  $\alpha = 17.04^{\circ}$ , 18.68° and 19.41° can be attributed to the (1 0 0), (0 0 2) and (1 0 1) hexagonal planes of Tl. The extra peaks at  $\alpha = 18.17^{\circ}$ , 21.92° and 22.30° could not be indexed to bulk Tl, Sb or In.

#### $Tl_xSb_y$ compounds

The extra peaks at  $\alpha = 18.17^{\circ}$ , 21.92° and 22.30° in the reflectivity ridge scan could be produced by the formation of Tl-Sb compounds. Two Tl-Sb compounds are known to exist: thallium antimonide, TlSb, which crystallises in a cubic, caesium chloride structure with a lattice parameter,  $a_{\text{TlSb}}$ , of 3.86Å (see figure 5.25); and Tl<sub>7</sub>Sb<sub>2</sub> which crystallises in a complex, many-atom basis, cubic structure with a lattice parameter,  $a_{\text{Tl}_7\text{Sb}_2}$ , of 11.618Å (see figure 5.26). The spacings between the cubic (H K L) planes of both  $Tl_xSb_y$  compounds are:

$$d_{HKL} = \frac{a}{\sqrt{H^2 + K^2 + L^2}} \tag{5.24}$$

The cubic reflections can be converted to the tetragonal scattering vectors of InSb using equation 5.15.



Figure 5.25: The bulk unit cell of cubic thallium antimonide (TlSb) (Tl - white, Sb - red)

Table 5.3 summarises the allowed reflections for  $\text{Tl}_{x}\text{Sb}_{y}$  and gives the relative intensity and corresponding h value for each reflection.

The in-plane diffraction peaks at h = 1.66 and k = 1.634 peaks were initially attributed to the (0 0 2) thallium planes (h = k = 1.652). Table 5.3 also shows that (1 1 0) TISb planes and the (3 3 0) Tl<sub>7</sub>Sb<sub>2</sub> planes also produce intense peaks at h or k = 1.672 and



Figure 5.26: The bulk unit cell of cubic Tl<sub>7</sub>Sb<sub>2</sub> (Tl - magenta, Sb - orange)

$Tl_xSb_y$	H	K		$d_{HKL}$	Intensity	$h \text{ or } k \ (l = 0.1)$
TlSb	1	0	0	3.860Å	69.2	1.178
TlSb	1	1	0	2.729Å	1000	1.672
TlSb	1	1	1	2.229Å	25.8	2.051
TlSb	2	0	0	1.930Å	197.6	2.369
TlSb	2	1	0	1.726Å	39.8	2.650
a Tos e				h mad my	incorel-spin	a server and the
$\mathrm{Tl}_7\mathrm{Sb}_2$	3	3	0	2.738Å	1000	1.667

Table 5.3: The relative strength and reciprocal-space location of  $Tl_xSb_y$  powder diffraction peaks

1.667 respectively. No Tl<sub>x</sub>Sb<sub>y</sub> reflections fit the specular reflectivity peaks at  $\alpha = 21.92^{\circ}$  or 22.3°.

#### $Tl_xO_y$ based compounds

Thallium is known to be readily oxidised. Care was taken to ensure that the Tl evaporators were heavily outgassed before growth, but the possibility still exists that thallium oxide was deposited on the InSb surface. Table 5.4 summarises the allowed reflections for the oxides of thallium (tetragonal Tl<sub>2</sub>O and cubic Tl<sub>2</sub>O<sub>3</sub>) and gives the relative intensity and corresponding h value for each reflection.

					-	
$Tl_xO_y$	H	K	L	$d_{HKL}$	Intensity	$h \text{ or } k \ (l = 0.1)$
Tl <sub>2</sub> O	0	0	6	6.307Å	43.4	0.713
$Tl_2O$	0	0	12	3.153Å	590.6	1.446
$Tl_2O$	1	0	1	3.035Å	69.2	1.503
$Tl_2O$	0	1	2	3.006Å	287	1.517
Tl <sub>2</sub> O	1	0	4	2.899Å	102.6	1.574
$Tl_2O$	0	1	5	2.825Å	1000	1.616
$Tl_2O_3$	2	0	0	5.267Å	1.6	0.858
$Tl_2O_3$	2	1	1	4.301Å	85.4	1.056
$Tl_2O_3$	2	2	2	3.041Å	1000	1.500
$\mathrm{Tl}_{2}\mathrm{O}_{3}$	4	0	0	2.634Å	391.6	1.734
Tl <sub>2</sub> O <sub>3</sub>	4	1	1	2.483Å	57.2	1.840

Table 5.4: The relative strength and reciprocal-space location of  $Tl_xO_y$  powder diffraction peaks

The most intense  $Tl_2O$  peak, the (0 1 5) reflection, is produced by a layer spacing of 2.825Å. This provides a possible match for the previously unaccounted peak in the

reflectivity ridge scan at  $\alpha = 18.17^{\circ}$ . The peaks at  $\alpha = 21.92^{\circ}$  and  $22.30^{\circ}$  are not reproduced by bulk Tl, bulk Sb, bulk In, TlSb, Tl<sub>7</sub>Sb<sub>2</sub> or the known oxides of Tl.

In summary, the extra in-plane peaks are attributed to either bulk Tl, TlSb or  $Tl_7Sb_2$  compounds, which would indicate a complex interface layer between the InSb(001)-c(4×4) reconstruction and the deposited Tl, with the formation of Tl-Sb bonds in either the TlSb or  $Tl_7Sb_2$  configuration. The extra reflectivity ridge scan peaks are attributed to bulk Tl and to  $Tl_2O$  which is readily formed. After completion of the bulk thallium wetting layer, Stranski-Krastanow 3-D island growth occurs.

# 5.5 Conclusions

A prerequisite for the growth of  $In_{1-x}Tl_xSb$  on the  $InSb(001)-c(4\times4)$  surface reconstruction is the growth of Tl on InSb. This aids the understanding of the atomic interactions between Tl and Sb and the preferred formation of Tl-Sb based compounds. The necessary starting point for the growth of Tl on InSb is the formation of a well ordered  $InSb(001)-c(4\times4)$  surface reconstruction. We have developed an Ar<sup>+</sup> ion bombardment and annealing cleaning technique to produce atomically clean, well formed  $InSb-c(4\times4)$ reconstructions using Sb capped and uncapped wafers.

The presence of symmetric, in-plane x-ray diffraction peaks in measurements on the "asloaded" capped samples showed that there was no preferential alignment of the amorphous antimony capping layer with respect to the substrate. Analysis showed that the weak and strong diffraction peaks at h = 1.2 and 1.47 are produced by the hexagonal (0 0 3) and (0 1 2) planes of Sb. A substantial re-ordering of the Sb cap at 180°C was observed during the first low temperature anneal by monitoring the intensity of the (1.47 0 0.1) in-plane amorphous Sb peak. This indicates that the antimony atoms have increased mobility at this temperature, sufficient thermal energy is available to align neighbouring Sb crystallites. On cooling, the new, larger crystallites contribute a greater amount to the in-plane Sb diffraction peaks. The optimum cleaning and decapping procedure was found to be a short 30 minute sputtering cycle of 900 eV Ar<sup>+</sup> ions (2–3  $\mu$ A beam current) followed by a rapid thermal desorption of the antimony cap under an antimony overpressure. Above 250°C a gradual depletion of antimony was observed. At approximately 305°C a more dramatic antimony loss was measured. An AES scan performed immediately after the decapping procedure showed a clean surface with a peak-to-peak In : Sb ratio of approximately 1 : 1.2. Our results are consistent with the measurements of Jones [62], who measured an Sb desorption temperature of 300°C and a similar In : Sb ratio for the Sb-rich c(4×4) reconstruction. The lack of surface contamination for the decapped sample proves that a 1000Å Sb cap is sufficient to protect the MBE grown highly ordered InSb buffer layer from oxidation during atmospheric exposure or low vacuum (10<sup>-3</sup>mbar) conditions for periods of up to a year.

Decapped surface prepared in this manner had atomic cleanliness comparable to uncapped surface prepared using  $Ar^+$  ion bombardment at elevated temperature. However, the process of sputtering the uncapped samples to remove surface impurities creates significant disordering and  $Ar^+$  ion incorporation at the sample surface. These effect are reduced, but not negated, by bombarding the sample at elevated sample temperature (approximately 350°C) [68]. For these reasons, Sb capping and subsequent decapping is the preferred method for preparing atomically clean, highly ordered surface reconstructions.

The InSb anti-phase x-ray position was monitored throughout the room temperature growth Tl on InSb(001)-c(4×4). In-plane and out-of-plane (specular reflectivity ridge scan) x-ray diffraction and AES measurements were used to characterise the structure of the MBE grown Tl layers. A calculation in which the thallium atoms initially form a new layer above the top, partially filled (0.75 ML) Sb layer fitted the initial decrease in the experimentally measured anti-phase intensity during room temperature deposition of Tl on the InSb-c(4×4) reconstruction. In contrast, calculations modelling the completion of the top partially occupied Sb layer before the formation of a new Tl layer produced an initial increase in intensity. The spacing between the top Sb layer and the first Tl layer and the Tl interplanar spacing was consistent with the bulk thallium interplanar spacing of 2.7625Å. The theoretical deposition rate was matched to the experimental completion rate of 1 ML in approximately 40 minutes. The lack of well formed oscillations in the room temperature growth curve after the completion of the first thallium layer indicates the formation of a wetting layer followed by disordered 3-D island growth (Stranski-Krastanow (SK) mode) rather than well ordered layer-by-layer Frank-van der Merwe (FM) growth. A reflectivity scan after Tl deposition showed the InSb Bragg reflection at  $\alpha = 15.97^{\circ}$  and extra peaks at  $\alpha = 17.04^{\circ}$ , 18.68° and 19.41° produced by the (1 0 0), (0 0 2) and (1 0 1) planes of Tl. An additional peak at  $\alpha = 18.17^{\circ}$  was produced by Tl<sub>2</sub>O. Other peaks at  $\alpha = 21.92^{\circ}$  and 22.30° are not consistent with either bulk Tl, bulk In, bulk Sb, TlSb,  $Tl_7Sb_2$ ,  $Tl_2O$  or  $Tl_2O_3$ . In-plane x-ray diffraction peaks at h = 1.66 and k = 1.634 can be attributed to either the  $(0\ 0\ 2)$  thallium planes (h = k = 1.652), the  $(1\ 1\ 0)$  TlSb planes (h = k = 1.672) or the (3 3 0) planes of Tl<sub>7</sub>Sb<sub>2</sub> (h = k = 1.667). A peak at k = 1.721 can be attributed to the  $(1 \ 0 \ 1)$  plane of Tl. The lack of a  $(1 \ 0 \ 1)$  Tl peak in the h direction shows a preferential alignment of the Tl domains. The levels of oxygen and carbon based contamination of the Sb rich surface reconstruction, the Tl-Sb interface region and the Tl film were below the detectable limit of AES.

Chapter 6

# The atomic structure of the $GaSb(001)-c(2 \times 6)$ surface reconstruction

## 6.1 Introduction

Gallium antimonide (which has a lattice constant of 6.0959Å at room temperature) belongs to the technologically important 6.1Å family of III-V binary semiconductor compounds, which includes InAs and AlSb. The lattice match between these compounds and the ternary and quaternary combinations allows tremendous flexibility in the design of opto-electronic devices. InAsSb, AlGaAsSb, GaInAsSb, InAs and AlSb are all closely lattice matched to GaSb and are used for a wide range of applications including: opto-electronic superlattices [76]; solar and thermophotovoltaic cells [77]; infrared light emitting diodes (LEDs) [78]; quantum well [79] and quantum dot [80] lasers; and detectors and position sensors to monitor tire tread deformation [81]!

The quaternary semiconductor GaInAsSb has attracted much interest due to its use as an infrared detector. GaInAsSb alloys have direct bandgaps of between 0.87–12  $\mu$ m, which cover the full range of infrared wavelengths. Detectors manufactured from alloys of GaInAsSb lattice matched to GaSb form heterojunctions which respond to a wavelength range of 1.7–4.3, making them sensitive to the short and mid-wavelength infrared range [82].

Reflectance difference spectroscopy (RDS) and x-ray diffraction have been used to characterise the structural properties of GaAsSb / GaSb superlattices [83]. Similarly, x-ray diffraction and secondary mass ion spectroscopy (SIMS) have been used to study AlGaSb layers on GaSb [84].

Ab-initio calculations using the local spin density approximation [85] predict the production of a dilute ferromagnetic semiconductor by the incorporation of small amounts of Mn into a GaSb matrix. Using MBE growth, an experimental incorporation of 3% Mn in (Ga,Mn)Sb has been achieved [86], producing a material combining magnetic and semiconducting properties for use in the "spintronics" revolution.

Despite the promising nature of there compounds, noticeable differences between the

MBE growth on vicinal surfaces of GaSb and the industry standard GaAs have been detected. This has been attributed to the increased mobility of Ga adatoms on the GaSb surface rather than on the GaAs surface and a higher sticking co-efficient for Ga adatoms at GaSb step edges. Different reconstructions are also detected during growth: " $(1\times3)$ " reconstructions for GaSb; and " $(2\times4)$ " reconstructions for GaAs [87].

The growth mode of many semiconductor materials is dependent on the morphology of the primary growth surface. Understanding the atomic topology of reconstructed semiconductor surfaces is essential for the production of nanoscale electronic devices. This is especially critical during the growth of highly ordered ultra-thin layers required for short-period superlattices and quantum well structures. For these reasons, there is a pressing need to understand the processes required to prepare atomically clean, highly ordered surface reconstructions extending over large domains.

We present the first synchrotron-based surface x-ray diffraction (SXRD) and Auger electron spectroscopy (AES) study of the optimal cleaning procedure for Sb capped and uncapped GaSb wafers. For the uncapped GaSb samples, the carbon and oxygen surface contamination was removed using argon ion bombardment at elevated sample temperature under an antimony overpressure, forming a weak GaSb(001)-"(1×3)" surface reconstruction. For the samples capped with a protective Sb capping layer, the carbon and oxygen surface contaminants were removed using argon ion bombardment at elevated sample temperature. The protective Sb cap was then thermally desorbed under an antimony overpressure, producing a well-ordered GaSb(001)-"(1×3)" reconstruction. Inplane and reflectivity x-ray diffraction scans were used to determine the surface ordering and the out-of-plane layer spacings for the c(2×6) surface reconstruction.

# 6.2 GaSb

#### 6.2.1 Bulk GaSb

Like many other III-V semiconductors gallium antimonide crystallises in the face centred cubic, zinc-blende structure. Each atom is tetrahedrally bonded to four atoms of the opposite atomic species. Group III antimony atoms occupy the face centred sites and the group V gallium atoms occupy the tetrahedral  $T^+$  sites (shown as red and green respectively in figure 6.1). The chemical bonds are neither purely covalent or purely ionic (the ionicity of GaSb is 0.33). GaSb is naturally p-type. The basis vectors which describe the cubic cell are:

$$\mathbf{A}_{1} = a_{0}\mathbf{i}$$
  

$$\mathbf{A}_{2} = a_{0}\mathbf{j}$$
  

$$\mathbf{A}_{3} = a_{0}\mathbf{k},$$
(6.1)

where the lattice constant of GaSb (at room temperature) is  $a_0 = 6.0959$ Å.

#### 6.2.2 Surface reconstructions of GaSb(001)

Depending on the conditions during growth of GaSb(001), two types of reconstruction are observed: the "1×5" reconstructions ((1×5), c(2×10) or (2×5)) between 350–400°C; and the "1×3" reconstructions ((1×3), (2×3) or c(2×6)) above 460°C.

Franklin [88] was the first to study the " $(1\times3)$ " reconstructions of GaSb(001) using HEED, STM and photoemission. Despite significant surface disorder, only the c $(2\times6)$  reconstruction was observed. They proposed that chains of antimony dimers, aligned along the [110] direction, were adsorbed onto an antimony terminated GaSb bulk.

Sieger [89] proposed two distinct models for the  $(1\times3)$  and the  $c(2\times6)$  reconstructions to fit RHEED and photoemission measurements. Both models contain Sb dimer chains in



Figure 6.1: Bulk GaSb

the top layer, the difference in the models occurs at the second layer of Sb atoms, a third of which have dangling surface bonds. In the  $c(2\times 6)$  reconstruction these bonds are satisfied by dimerisation. In the  $(1\times 3)$  reconstruction it is hypothesised that extra Ga atoms are incorporated to satisfy the Sb bonds. It is still unproven that the two hypothesised reconstructions are not actually a single reconstruction with varying degrees of surface disorder. They also measured the irreversible transition from the  $c(2\times 10)$  to the  $c(2\times 6)$  reconstruction at approximately  $375^{\circ}$ C.

Thibado [90] investigated other III-Sb(001) surfaces and showed, using STM, that InSb and AlSb both exhibit the insulating  $c(4\times4)$  reconstruction, consistent with the model proposed for the GaAs- $c(4\times4)$  surface. However, unlike any other III-V semiconductor, the GaSb(001) surface forms " $(1\times5)$ " reconstructions under group V rich, low temperature growth conditions. Whitman [91] has shown that the weakly metallic " $(1\times5)$ " reconstructions violate the electron counting model (ECM) which is widely used to determine a list of possible surface configurations. It is widely believed that polar semiconductor surfaces reconstruct such that:

- all the dangling bonds of the group V surface atoms are unoccupied
- all the dangling bonds of the group III surface atoms are doubly occupied

Violation of this principle implies that the ECM may not be universal for all III-V semiconductors. An explanation could be that the Sb-Sb homo-bond is stronger than the Ga-Sb hetero-bond, a property unique to GaSb among the III-Sb compounds. Barvosa-Carter [92] has recently proposed that the " $(1\times3)$ " reconstructions are composed of three distinct, kinked-dimer  $(4\times3)$  reconstructions, the relative frequency and arrangement dependent upon the surface dynamics.

#### The GaSb(001) surface unit cell

The (001) surface plane is conventionally described by the following set of basis vectors:

$$\mathbf{a}_{1} = \frac{1}{2}(\mathbf{A}_{1} - \mathbf{A}_{2}) = \frac{a_{0}}{2}(\mathbf{i} - \mathbf{j})$$
  

$$\mathbf{a}_{2} = \frac{1}{2}(\mathbf{A}_{1} + \mathbf{A}_{2}) = \frac{a_{0}}{2}(\mathbf{i} + \mathbf{j})$$
  

$$\mathbf{a}_{3} = \mathbf{A}_{3} = a_{0}\mathbf{k}$$
(6.2)

$$\begin{bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{bmatrix} = \begin{bmatrix} 0.5 & -0.5 & 0.0 \\ 0.5 & 0.5 & 0.0 \\ 0.0 & 0.0 & 1.0 \end{bmatrix} \begin{bmatrix} \mathbf{A}_1 \\ \mathbf{A}_2 \\ \mathbf{A}_3 \end{bmatrix}$$
(6.3)

$$|\mathbf{a}_1| = |\mathbf{a}_2| = \frac{a_0}{\sqrt{2}} = 4.3105\text{\AA}, |\mathbf{a}_3| = a_0 = 6.0959\text{\AA}$$
 (6.4)

The corresponding reciprocal lattice vectors are:

$$\mathbf{b}_{1} = \mathbf{B}_{1} - \mathbf{B}_{2} = \frac{2\pi}{a_{0}}(\mathbf{i} - \mathbf{j})$$

$$\mathbf{b}_{2} = \mathbf{B}_{1} + \mathbf{B}_{2} = \frac{2\pi}{a_{0}}(\mathbf{i} + \mathbf{j})$$

$$\mathbf{b}_{3} = \mathbf{B}_{3} = \frac{2\pi}{a_{0}}\mathbf{k}$$
(6.5)

$$|\mathbf{b}_1| = |\mathbf{b}_2| = \frac{2\pi}{a_0}\sqrt{2} = 1.45766 \text{\AA}^{-1}, |\mathbf{b}_3| = \frac{2\pi}{a_0} = 0.97019 \text{\AA}^{-1}.$$
 (6.6)

The transformation between surface and bulk reciprocal space co-ordinate systems is derived as:

$$h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 = H\mathbf{B}_1 + K\mathbf{B}_2 + L\mathbf{B}_3, \tag{6.7}$$

$$\begin{bmatrix} h & k & l \end{bmatrix} \begin{bmatrix} 0.5 & -0.5 & 0.0 \\ 0.5 & 0.5 & 0.0 \\ 0.0 & 0.0 & 1.0 \end{bmatrix} = \begin{bmatrix} H & K & L \end{bmatrix}$$
(6.8)

where lower and upper case letters indicate surface and bulk systems respectively.

# 6.2.3 GaSb-c $(2\times 6)$

The atomic model for the GaSb-c(2×6) surface proposed by Sieger [89], in basic agreement with the model proposed by Resch-Esser [93]. Parallel rows of Sb dimers in the top layer extend along the  $[1\overline{10}]$  direction, separated by staggered dimers in the second Sb layer. The alternate ordering of these staggered dimers forms the c(2×6) symmetry (see figure 6.2). The surface lattice vectors,  $\mathbf{a}_{1}^{*}$ , which characterise the c(2×6) surface unit cell are:

$$\mathbf{a}_{1}^{\star} = \mathbf{a}_{1} + 3\mathbf{a}_{2} = a_{0}(2\mathbf{i} + \mathbf{j}) 
 \mathbf{a}_{2}^{\star} = -\mathbf{a}_{1} + 3\mathbf{a}_{2} = a_{0}(\mathbf{i} + 2\mathbf{j}) 
 \mathbf{a}_{3}^{\star} = \mathbf{a}_{3} = a_{0}\mathbf{k}$$
(6.9)

$$\begin{bmatrix} \mathbf{a}_{1}^{\star} \\ \mathbf{a}_{2}^{\star} \\ \mathbf{a}_{3}^{\star} \end{bmatrix} = \begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{A}_{1} \\ \mathbf{A}_{2} \\ \mathbf{A}_{3} \end{bmatrix}$$
(6.10)

The lengths of the  $c(2 \times 6)$  surface lattice vectors are:

$$|\mathbf{a}_{1}^{\star}| = |\mathbf{a}_{2}^{\star}| = \sqrt{5}a_{0} = 13.6309\text{\AA}, |\mathbf{a}_{3}^{\star}| = a_{0} = 6.0959\text{\AA}$$
 (6.11)
The corresponding  $c(2\times 6)$  reciprocal lattice vectors are:  $a_{1}$  and  $b_{2}$  and  $b_{3}$  are the second second

$$\mathbf{b}_{1}^{\star} = \frac{2\pi}{3a_{0}}(2\mathbf{i} - \mathbf{j}) = \frac{1}{2}\mathbf{b}_{1} + \frac{1}{6}\mathbf{b}_{2}$$
  

$$\mathbf{b}_{2}^{\star} = \frac{2\pi}{3a_{0}}(-\mathbf{i} + 2\mathbf{j}) = -\frac{1}{2}\mathbf{b}_{1} + \frac{1}{6}\mathbf{b}_{2}$$
  

$$\mathbf{b}_{3}^{\star} = \frac{2\pi}{a_{0}}(\mathbf{k})$$
(6.12)

$$|\mathbf{b}_{1}^{\star}| = |\mathbf{b}_{2}^{\star}| = \frac{2\pi}{3a_{0}}\sqrt{5} = 0.76826\text{\AA}^{-1}, |\mathbf{b}_{3}^{\star}| = \frac{2\pi}{a_{0}} = 1.03072\text{\AA}^{-1}.$$
 (6.13)



Figure 6.2: The GaSb(001)-c(2×6) surface cell showing bulk gallium and antimony atoms (green and red respectively), dimerisation of antimony atoms in the second antimony layer (yellow) and antimony dimers in the top layer (blue). The c(2×6) and the (1×1) surface cells and the bulk unit cell are indicated in blue, red and green respectively

The reciprocal space reflections for the  $(1 \times 1)$  unit vectors,  $\mathbf{b}_i$ , and the  $c(2 \times 6)$  reciprocal vectors,  $\mathbf{b}_i^*$ , are illustrated in figure 6.3.



Figure 6.3: The reciprocal space reflections for the GaSb(001)-c(2×6) reconstruction in terms of the (1×1) unit vectors,  $\mathbf{b}_i$ , and the c(2×6) reciprocal vectors,  $\mathbf{b}_i^*$ 

### 6.2.4 GaSb(001)-(2x3)

In the proposed GaSb(001)-(2x3) structure, the staggered dimers in the second Sb layer are aligned parallel to the [110] direction (shown in figure 6.4). The surface lattice vectors,  $\mathbf{a}_1^+$ , which characterise the (2×3) surface unit cell are:

$$\mathbf{a}_{1}^{+} = 2\mathbf{a}_{1} = a_{0}(\mathbf{i} - \mathbf{j}) 
\mathbf{a}_{2}^{+} = 3\mathbf{a}_{2} = \frac{3a_{0}}{2}(\mathbf{i} + \mathbf{j}) 
\mathbf{a}_{3}^{+} = \mathbf{a}_{3} = a_{0}\mathbf{k}$$
(6.14)

and to monitor the formation of the Ga5b/001)-c(2×6) reconstruction

$$\begin{bmatrix} \mathbf{a}_{1}^{+} \\ \mathbf{a}_{2}^{+} \\ \mathbf{a}_{3}^{+} \end{bmatrix} = \begin{bmatrix} 1 & -1 & 0 \\ 1.5 & 1.5 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{A}_{1} \\ \mathbf{A}_{2} \\ \mathbf{A}_{3} \end{bmatrix}$$
(6.15)

The lengths of the  $(2 \times 3)$  surface lattice vectors are:

$$|\mathbf{a}_{1}^{+}| = \sqrt{2}a_{0} = 8.6209\text{\AA}, |\mathbf{a}_{2}^{+}| = \frac{3\sqrt{2}}{2}a_{0} = 12.93136\text{\AA}, |\mathbf{a}_{3}^{+}| = a_{0} = 6.0959\text{\AA}$$
(6.16)

The corresponding  $(2 \times 3)$  reciprocal lattice vectors are:

$$\mathbf{b}_{1}^{+} = \frac{\pi}{a_{0}}(\mathbf{i} - \mathbf{j}) = \frac{1}{2}\mathbf{b}_{1} 
\mathbf{b}_{2}^{+} = \frac{2\pi}{3a_{0}}(\mathbf{i} + \mathbf{j}) = \frac{1}{3}\mathbf{b}_{2} 
\mathbf{b}_{3}^{+} = \frac{2\pi}{a_{0}}\mathbf{k}$$
(6.17)

$$|\mathbf{b}_{1}^{+}| = \frac{\sqrt{2}\pi}{a_{0}} = 0.7288 \text{\AA}^{-1}, |\mathbf{b}_{2}^{+}| = \frac{2\sqrt{2}\pi}{3a_{0}} = 0.4859 \text{\AA}^{-1}, |\mathbf{b}_{3}'| = \frac{2\pi}{a_{0}} = 1.0307 \text{\AA}^{-1} \quad (6.18)$$

The reciprocal space reflections for the  $(1 \times 1)$  unit vectors,  $\mathbf{b}_i$ , and the  $(2 \times 3)$  reciprocal vectors,  $\mathbf{b}_i^+$ , are illustrated in figure 6.5.

## 6.3 Experimental

The major objectives of the experiment were:

- to characterise the Sb capping layer;
- produce a contaminant free surface;
- to observe the surface morphology as the protective Sb cap was desorbed;
- and to monitor the formation of the  $GaSb(001)-c(2\times 6)$  reconstruction.



Figure 6.4: The GaSb(001)- $(2\times3)$  surface cell showing bulk gallium and antimony atoms (green and red respectively), dimerisation of antimony atoms in the second antimony layer (yellow) and antimony dimers in the top layer (blue). The  $(2\times3)$  surface cell is indicated in blue



Figure 6.5: The reciprocal space reflections for the GaSb(001)-(2×3) reconstruction in terms of the (1×1) unit vectors,  $\mathbf{b}_i$ , and the (2×3) reciprocal vectors,  $\mathbf{b}_i^+$ 

### 6.3.1 MBE growth of Sb capped and uncapped GaSb samples

Circular (3 inch diameter), undoped p-type GaSb(001) wafers (Wafertech) were loaded into MBE chamber at QinetiQ, and annealed at 200°C for 18 hours. Prior to growth, the wafer was held under an antimony over-pressure and the substrate temperature,  $T_s$ , increased until the surface contaminants started to desorb ( $\approx$ 520°C) and a "(1×3)" reconstruction observed using RHEED. The substrate was stabilised at this temperature under an antimony flux, and annealed for ten minutes to fully remove the surface impurities (typically several tens of monolayers thick). The sample was then cooled to the growth temperature ( $T_s = T_t + 120$ °C) and a 2µm thick, high quality crystalline, undoped GaSb buffer layer grown under excess Sb conditions.  $T_t$  ( $\approx$  360°C) is the static transition temperature from the "(1×5)" to the "(1×3)" surface reconstruction. Optionally, an undoped 500–1000Å thick Sb protective cap was grown at  $T_s = 150$ °C. Under typical growth conditions, the antimony source deposits sufficient antimony to grow 1.6 monolayers (ML) per second of GaSb on a gallium rich surface. Correspondingly, the gallium source will deposit enough gallium to grow 0.95 ML per second of GaSb on an antimony rich surface. Using the above antimony and gallium deposition rates and a substrate temperature of  $T_t + 120^{\circ}$ C (460°C) highly ordered GaSb, can be deposited at 0.9 ML per second. One ML of GaSb(001) corresponds to 3.048 Å; therefore a growth rate of 0.9 ML per second equates to 2.743 Å per second. A total deposition time of approximately two hours is required to grow a  $2\mu$ m layer of GaSb. After the required deposition period, the gallium shutter was closed and the sample cooled to  $T_t$ . The antimony shutter was closed when a clear (1×5) RHEED pattern was observed. Finally, the sample was cooled to room temperature. The prepared wafer was then unloaded from the growth system and viewed using a microscope: no macroscopic defects were detected. Compounds containing arsenic are routinely produced within the MBE growth chamber at QinetiQ, leading to a small arsenic contamination of the highly ordered GaSb layer.

Sb capped and uncapped samples were transported to Leicester and stored under low vacuum.  $8 \times 8$ mm cleaved sections of the GaSb wafers were bonded to thoroughly outgassed  $10 \times 8$ mm molybdenum backing plates using a small amount of molten indium. The samples were then mounted on a sample holder and transferred via the sample transfer port into the SXRD UHV chamber.

The LUXC chamber was coupled (via a differentially pumped rotary seal) to the 6-circle diffractometer at station 9.4 of the SRS at Daresbury. The x-ray measurements were made using x-rays with a wavelength of 1.22Å (energy = 10.171 keV) and detected using a liquid nitrogen cooled, solid state germanium detector. The end of beam, pre-sample, slits were set to define the incident x-ray beam to be 2mm (horizontally) × 1mm (vertically). The post sample slits (which define the active area on the sample surface observed by the detector) and the detector slits (which define the l resolution of the diffracted beam) were set to 10mm (horizontally) × 2mm (vertically) and 5mm (horizontally) × 10mm (vertically) respectively.

A comprehensive account of the LUXC chamber, the 6-circle diffractometer at station

9.4, and the procedure used to mount the cleaved wafer sections is given in section 3.3.

## 6.4 Results and discussion

### 6.4.1 Uncapped GaSb samples

AES measurements of the "as-loaded" uncapped sample before and after cleaning

After loading an uncapped GaSb(001) sample into the SXRD UHV chamber, an initial Auger scan was performed (Figure 6.6). Antimony and gallium peaks were observed, along with oxygen and carbon surface contamination.



**Figure 6.6:** AES measurements of an uncapped GaSb sample before (black) and after annealing (red) under an Sb overpressure

# 6.4.2 Removal of surface contaminants from an uncapped GaSb sample

A number of strategies exist for producing clean, well ordered GaSb(001) surfaces:

- Thermal annealing. Temperatures between 500–600°C are required to thermally desorb the O and C based surface contaminants. Unfortunately, annealing above 450° leads to preferential Sb desorption, forming Ga rich surface domains. Further annealing to above 500° irreversibly forms Ga droplets on surface. No clean, ordered GaSb(001) reconstructions can be formed using this method.
- Thermal annealing under an Sb flux. An overpressure of Sb (typically 10<sup>-4</sup> mbar) during high temperature anneals is required to maintain the Ga:Sb surface stoichiometry, resulting in semi-clean (oxygen contaminants are removed, leaving residual carbon contaminants), forming surface reconstructions, albeit with significant surface roughness [94].
- Cycles of thermal annealing under an Sb flux and low energy Ar<sup>+</sup> ion bombardment. Bombardment is much more effective for the removal of C contaminants. Lower temperature annealing lead to reduced surface roughness and better quality, larger domain reconstructions.
- Hydrogen Plasma Treatment (HPT): successful cleaning, but residual energetic ions present produce surface and subsurface modifications. Homogeneity is a prerequisite for device production.
- Atomic Hydrogen Cleaning (AHC): Lower substrate temp 400–470°C than purely thermal annealing required to remove O contamination. Sb desorption still. A two-stage, low temperature (maximum 300°C) AHC treatment, which may solve the high anneal temperature problem, has recently been proposed [95]. High resolution electron energy loss spectroscopy (HREELS) and synchrotron radiation

photoemission spectroscopy (SRPES) revealed surfaces superior to those produced by sputtering an annealing.

An initial test was to determine if the surface contaminants could be thermally desorbed. The sample was slowly annealed, under an antimony overpressure, whilst monitoring the peak to peak height of the oxygen peak in the Auger spectrum (Figure 6.4.2).



Figure 6.7: AST scan monitoring the oxygen surface contamination of an uncapped GaSb sample during annealing

As expected, the oxygen component of the surface contamination decreases as the sample is warmed from room temperature to approximately 200°C. Above this level, the oxygen level due to outgassing from the molybdenum backing plate. Above 400°C the oxygen level slowly decreases. When the sample temperature reached approximately 495°C there was a sudden reduction in the oxygen signal, at which stage the Sb evaporator shutter was opened. An almost identical oxide desorption temperature was observed in the QinetiQ MBE chamber. An Auger scan showed the removal of the majority of the oxygen contamination, the sharpening of the Sb features at 454 and 463 eV but the remains of the carbon peak.

Sample temperature	Sb : C ratio
140°C	1: 0.4
465°C	1: 0.27
545°C	1: 0.248
620°C	1: 0.315
Cooled to room temperature	1: 0.25

To determine if the carbon could be thermally desorbed, the sample was again heated under an Sb flux and the Auger Sb : C peak-to-peak ratio monitored (see table 6.1).

**Table 6.1:** The Auger Sb : C peak-to-peak ratio as a function of temperatureduring a high temperature anneal under an Sb overpressure

Analysis of table 6.1 shows, as expected, the decrease of the Sb : C ratio as the sample is heated. However, above 550°C the ratio increases as antimony is preferentially depleted from the sample surface even under an Sb overpressure. On cooling the sample to room temperature, visual inspection showed regions at the edge of the sample had melted (the melting temperature of GaSb is 712°C). This showed that carbon based compounds can not be removed by thermal annealing.

Figure 6.8 shows AES measurements of the uncapped sample before and after  $Ar^+$  bombardment and annealing. Intermediate AES results after the  $Ar^+$  bombardment, but before the anneal, showed a total removal of the carbon contamination. The presence of carbon after the anneal shows either contamination from the heater filament or diffusion of contamination from the GaSb bulk.

### 6.4.3 Sb capped GaSb samples

Group V capping is a standard technique used on a number of binary and ternary III– V semiconductors including GaAs [96] and InAlSb(100) [97]. An Sb protective capping layer is deposited on top of the GaSb buffer layer in the MBE chamber. This cap can



Figure 6.8: AES from an uncapped sample before and after  $Ar^+$  bombardment and annealing, showing the reduction of carbon and oxygen contamination during the cleaning process

subsequently be removed by thermal desorption under UHV conditions.

#### AES measurements of "as loaded" capped samples

During the UHV chamber bake-out it is standard practise to out-gas the samples at intermediate temperatures for prolonged periods of time (24 hours at 250°C). However, for these samples it was observed that during the decapping procedure, the oxygen surface contamination level, measured using AES, remained constant. This indicates that the protective antimony capping layer had been fully oxidised during bake-out. AES measurements of thermally decapped wafers by Dumas [98] and Goletti [99], without prior sputtering, showed the removal of oxygen based contaminants, but carbon contamination levels remained comparable to those measured before decapping. This shows that any carbon based contaminants on the substrate migrate to the decapped sample surface during decapping. To ensure the integrity of the cap, samples were bonded to heavily outgassed backing plates and transferred to the UHV chamber via the sample transfer port. Prior to decapping, no heating was applied to the samples. Figure 6.9 shows the contaminants of "as-loaded" uncapped wafer using AES. Low energy AES scans did not reveal any trace of Ga, in agreement with Goletti [99] who used Raman spectroscopy and AES to verify the integrity of the 1800Å Sb capping layer grown at 200°C. However, although the Sb cap deposited by Dumas [98] was believed to be 2000–3000Åthick, the presence of Ga was detected using AES, indicating that his capping layer, grown whilst cooling the sample to room temperature, may have been as thin as 100Å in places. We can conclude that more homogeneous Sb caps are formed by depositing Sb at an elevated substrate temperature of 150–200°C.



Figure 6.9: AES measurements of an Sb capped GaSb sample before (black) and after  $Ar^+$  ion bombardment (red and blue), showing the removal of oxygen and carbon based contaminants

### Removal of surface contaminants from an Sb capped sample

Two twenty minute bombardment cycles of 900eV Ar<sup>+</sup> ions (1–2  $\mu$ A beam current) were sufficient to remove the majority of the carbon and oxygen based surface contamination (from a Sb : C : O ratio of 1 : 0.47 : 0.93 before to a 1 : 0.2 : 0.08 after bombardment), leaving a clean antimony auger signal produced by the capping layer (shown in red in figure 6.9). Our measurements indicate that removal of the surface contamination from GaSb is much more difficult than from InSb.

#### X-ray measurements before the decapping procedure

Prior to the decapping procedure, the sample was aligned crystallographically (described in section 5.4.1) and in-plane measurements with a fixed incident x-ray angle of  $1.7^{\circ}$ (corresponding to l = 0.3, eliminating critical angle variations) were performed. A (0 k 0.3) x-ray scan along the  $\mathbf{b}_2$  direction showed strong reflections at k = 1.37 and 2.77, and weaker reflections at k = 0.62 and 1.69 (shown in red in figure 6.10). An in-plane scan along the  $\mathbf{b}_2$  direction only showed strong peaks at h = 1.37 and 2.77, with no peaks at h = 0.62 and 1.69.



Figure 6.10: In-plane (0 k 0.3) x-ray scans along the  $\mathbf{b}_2$  direction, before (red) and after (black) a low temperature anneal

The structure of antimony was discussed in section 5.4.1. Using equation 5.15 the location

H	K	L	-H + K + L	$d_{HKL}$	Intensity	$k \ (h = 0,  l = 0.3)$
0	0	3	3	3.758Å	27.6	1.132
1	0	1	0	$3.542 \text{\AA}$	8.1	1.203
0	1	2	3	3.111Å	1000	1.374
1	0	4	3	2.249Å	387	1.912
1	1	0	0	$2.154\text{\AA}$	375	1.998
2	0	2	0	1.771Å	203.2	2.434
0	2	4	6	1.556Å	124.8	2.774
1	1	6	6	1.416Å	80.6	3.049
1	2	2	3	1.368Å	84.4	3.156

of the antimony peaks can be calculated. Table 6.2 summarises the allowed reflections for antimony and gives the relative intensity and corresponding k value for each reflection.

Analysis of table 6.2 shows that the strong diffraction peaks at k = 1.37 and 2.77 are produced by the hexagonal (0 1 2) and (0 2 4) Sb reflections.

### Removal of the amorphous Antimony cap

Two methods are available to desorb the Sb cap: low temperature annealing (200°C) for extended periods of time; or rapid, high temperature (up to 350°C) annealing. The former method produces heavily contaminated surfaces. The most effective method of removing the amorphous antimony cap, proposed by Dumas [98], is to rapidly heat the sample to 300°C and anneal for up to 30 minutes, producing diffraction patterns superior to uncapped surfaces prepared using sputtering and annealing. Above 350°C, there is a rapid preferential loss of Sb, irreversibly producing a disordered, Ga rich environment, characterised by microscopic Ga droplets. Resch-Esser [93] also reported the microscopic structure of  $c(2\times6)$  surfaces prepared by antimony decapping using LEED and STM.

Prior to decapping, the x-ray detector and diffractometer were positioned to monitor the (0 1.37 0.3) antimony peak during the thermal desorption procedure. Desorption was carried out under an antimony over-pressure (the Sb Knudsen cell evaporator was heated to 430–460°C, producing a vapour pressure of  $10^{-5}$ – $10^{-4}$  Torr) to maintain the Ga : Sb surface stoichiometry, ensuring the surface did not become irreversibly Ga rich.



Figure 6.11: Monitoring the (1.37 0 0.3) amorphous antimony diffraction peak during a low temperature sample anneal, showing a re-ordering of the protective
Sb capping layer at around 190°C

Analogous to the low temperature anneal of antimony capped InSb, a substantial reordering of the Sb cap was observed at around 190°C (see figure 6.11). Arsenide is known to grow amorphously on GaAs(001) but Sb layers form polycrystalline regions on GaSb after approximately 20 MLs. During a low temperature anneal (less than 300°C) Goletti [99] also measured facet LEED spots indicating polycrystallinity formation of the Sb cap. Full desorption of the cap was measured at 310°C under an Sb overpressure (comparable to the slightly higher desorption temperature of 370°C measured by Goletti [99]). Figure 6.12 shows the gradual depletion of the Sb capping layer (identified by the reduction in the intensity of the Sb peaks at k = 1.37 and 2.77) and the formation of the "(1×3) surface reconstruction characterised by peaks at k = n / 3.



Figure 6.12: Formation of the  $c(2 \times 6)$  surface reconstruction as the antimony cap is desorbed under an antimony flux. This is indicated by the reduction of the antimony peaks at k = 1.37 and 2.77 and the formation of third order reconstruction peaks

Figures 6.13,6.14, 6.15 and 6.16 show  $(0 \ k \ 0.3)$ ,  $(0.5 \ k \ 0.3)$  and  $(1.0 \ k \ 0.3)$  in-plane x-ray scans along the  $\mathbf{b}_2$  direction and a  $(h \ 0 \ 0.3)$  in-plane x-ray scan along the  $\mathbf{b}_1$  direction respectively. Sharp, intense peaks are observed at  $n \ / 3$  in the  $(0 \ k \ 0.3)$  and  $(1.0 \ k \ 0.3)$ scans (figures 6.13 and 6.15). Weaker features are observed at  $n \ / 2$  in the  $(h \ 0 \ 0.3)$  scan (figure 6.16). This indicates that the surface reconstruction has a " $(2\times3)$ " periodicity. To determine if the reconstruction is  $(2\times3)$  or  $c(2\times6)$  a  $(0.5 \ k \ 0.3)$  scan was performed. This showed weak peaks at  $k = (1 + 2n) \ / 6$ . Analysis of the reciprocal space reflections for the  $c(2\times6)$  and the  $(2\times3)$  reconstruction was  $c(2\times6)$ . The relative strengths of the intense third order peaks in the  $\mathbf{b}_2$  direction and the much weaker half order peaks in the  $\mathbf{b}_1$  direction are consistent with measurements carried out by Franklin [88].



Figure 6.13: In-plane (0 k 0.3) x-ray scan along the  $\mathbf{b}_2$  direction, showing third order  $\mathbf{c}(2\times 6)$  surface reconstruction peaks at k = n / 3



Figure 6.14: In-plane (0.5 k 0.3) x-ray scan along the  $\mathbf{b}_2$  direction, showing weak third order  $c(2\times 6)$  surface reconstruction peaks at k = (1 + 2n) / 6



**Figure 6.15:** In-plane (1.0 k 0.3) x-ray scan along the  $\mathbf{b}_2$  direction, showing third order  $c(2\times 6)$  surface reconstruction peaks at k = n / 3

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Figure 6.16: In-plane  $(h \ 0 \ 0.3)$  x-ray scan along the  $\mathbf{b}_1$  direction, showing extremely weak half order  $c(2\times 6)$  surface reconstruction peaks at h = n / 2

### 6.4.4 Modelling the reconstruction

A full set of reflectivity scans were performed to determine the out-of-plane structure of the reconstruction. The surface normal of the sample was aligned perpendicular to the incident x-ray beam. For each incident angle the detector was scanned through the specular reflected beam and the total intensity integrated numerically. This procedure was repeated for a range of incident angles. A number of correction factors were applied to the integrated intensity values:

- Attenuation. Lead and aluminium filters are required for small angles of incidence and in the vicinity of the (0 0 2) Bragg peak to stop the detector overloading and responding non-linearly. Normalisation is achieved by performing identical scans with different levels of attenuation.
- Beam decay. Detector counts are normalised to the temporal decay of the beam by dividing by the number of monitor counts detected by an ionisation chamber up-stream from the sample and multiplying by 100,000.
- Lorentz factor  $= \frac{1}{\sin 2\beta_{\text{in}}}$ , where  $\beta_{\text{in}}$  is the incident angle.  $\beta_{\text{in}} = \chi = \alpha/2$  in the  $\beta_{\text{in}} = \beta_{\text{out}}$  diffractometer mode.
- Polarisation factor =  $\cos \alpha^2$ .
- Illuminated sample area. The x-ray beam was defined to be 2mm in the horizontal plane. Given that the sample is 8mm wide, the incident angle at which the sample is "flooded" by the x-ray beam is χ = α/2 = 14.477°, corresponding to l = 2.5. Therefore all measurements below l = 2.5 need no illuminated area correction.

A full description of the polarisation and Lorentz factors is given in sections 3.7.1 and 3.7.2.

### Modelling the GaSb(001)-c $(2 \times 6)$

A generalised model for the  $c(2\times 6)$  surface reconstruction is shown in figure 6.2. Dimerisation of the top layer of antimony atoms (bonded to the second row of unreconstructed Sb atoms) and the second layer of Sb atoms (bonded to bulk Ga atoms) leads to in-plane and possible out-of-plane atomic displacements from the ideal bulk positions. Figure 6.17 shows a simplified surface model, illustrating the key features of the  $c(2\times 6)$  surface dimerisation.



Figure 6.17: Simplified model of the  $c(2\times 6)$  antimony surface dimerisation (bulk gallium - green, bulk antimony - red, first layer of antimony dimers - blue, second layer of antimony dimers - yellow)

The reflectivity from a model of the  $c(2\times 6)$  surface reconstruction was calculated using the structure factor calculation software ROD. The layer heights  $z_1$  (the vertical separation of the top Sb dimers from the second layer of bulk antimony atoms) and  $z_2$  (the vertical separation of the second layer of antimony dimers from the bulk gallium atoms) were fitted to achieve the optimum agreement with the experimental reflectivity. Figure 6.18 shows the experimental reflectivity and calculated reflectivity curves for models with the

bulk spacing and fitted values for  $z_1$  and  $z_2$ . Analysis shows that the top Sb layer of dimers and the second layer of antimony dimers are only marginally displaced from their bulk positions.



**Figure 6.18:** An experimental reflectivity scan of the GaSb-c( $2\times 6$ ) reconstruction and theoretical reflectivity curves for models with the bulk spacing and fitted values for  $z_1$  and  $z_2$ , shown in red and blue respectively

## 6.5 Conclusions

We have developed an  $Ar^+$  ion bombardment and thermal annealing cleaning technique for antimony capped and uncapped GaSb samples to produce well ordered, GaSb(001)c(2×6) surface reconstructions.

For uncapped samples we have shown that annealing at approximately 495°C, under an antimony overpressure, was sufficient to remove the oxygen component of the surface contamination. However, higher temperature anneals, up to the melting temperature of GaSb (712°C), were insufficient to remove the carbon contamination. AES measurements indicated that at these high temperatures, antimony was preferentially depleted from the

sample despite a large antimony overpressure of  $10^{-3}$  mbar.

For 1000Å thick antimony capped samples we observed no trace of gallium using low energy AES measurements, in agreement with Goletti [99] who used Raman spectroscopy and AES to verify the integrity of the 1800Å Sb capping layer grown at 200°C. However, although the Sb cap deposited by Dumas [98] was believed to be 2000–3000Å thick, the presence of Ga was detected using AES, indicating that his capping layer, grown whilst cooling the sample to room temperature, may have been as thin as 100Å in places. We can conclude that more homogeneous Sb caps are formed by depositing onto a substrate at an elevated temperature of between 150–200°C.

Long, low temperature sample anneals during the bake-out procedure of the UHV chamber have been shown to compromise the Sb cap. AES measurements during the decapping of samples treated in this manner revealed a constant carbon and oxygen contamination throughout the protective cap. To ensure the integrity of the Sb cap, samples were bonded to heavily outgassed Mo backing plates and transferred to the UHV chamber via the sample transfer port after bake-out. We have shown using this technique that a 1000Å Sb cap is sufficient to protect the MBE grown GaSb buffer layer from oxidation during atmospheric exposure for periods of up to a year.

After crystallographically aligning the samples, in-plane (0 k 0.3) surface x-ray diffraction scans along the  $\mathbf{b}_2$  direction showed strong antimony reflections at k = 1.37 and 2.77, and weaker reflections at k = 0.62 and 1.69. Perpendicular scans along the  $\mathbf{b}_2$  direction only showed strong peaks at h = 1.37 and 2.77, with no peaks at h = 0.62 and 1.69. The strong diffraction peaks at h and k = 1.37 and 2.77 are produced by the hexagonal (0 1 2) and (0 2 4) Sb reflections, indicating no preferred axis of alignment for the Sb cap. It is believed that the extra peaks at k = 0.62 and 1.69 are produced by carbon based forms of surface contamination.

Analogous to antimony capped InSb, a substantial re-ordering of the Sb cap was observed at around 190°C during a low temperature anneal by monitoring the (0 1.37 0.3) antimony peak. This substantiates our claim that antimony capping layers grown at elevated substrate temperatures of between 150–200°C are more homogeneous.

The optimum cleaning and decapping procedure was found to be a forty minute sputtering cycle of 900eV Ar<sup>+</sup> ions (1–2  $\mu$ A beam current) followed by a rapid thermal desorption of the antimony cap at 310°C under an Sb overpressure. An AES measurement performed immediately after the decapping procedure showed the removal of the majority of the carbon and oxygen based surface contamination (from an Sb : C : O ratio of 1 : 0.47 : 0.93 before cleaning, to a 1 : 0.2 : 0.08 after bombardment and decapping). It was noted that longer periods of sputtering were required to remove the surface contamination from GaSb compared to InSb.

In-plane (0 k 0.3) and (1.0 k 0.3) x-ray scans showed sharp, intense peaks at the third order positions (k = n / 3). Conversely, much weaker features were observed in ( $h \ 0 \ 0.3$ ) scans at the half order positions h = n / 2, indicating that the surface reconstruction has a "(2×3)" periodicity. To determine if the reconstruction is (2×3) or c(2×6) a (0.5 k 0.3) scan was performed. Measurement of the location of third order peaks in a (0.5 k 0.3) scan conclusively showed the symmetry of the reconstruction to be c(2×6) rather than (2×3). The relative strengths of the intense third order peaks in the b<sub>2</sub> direction and the much weaker half order peaks in the b<sub>1</sub> direction are consistent with measurements of the c(2×6) surface carried out by Franklin [88] using STM.

The reflectivity from a model of the  $c(2\times 6)$  surface reconstruction was calculated using the structure factor calculation software ROD. The layer heights  $z_1$  (the vertical separation of the top Sb dimers from the second layer of bulk antimony atoms) and  $z_2$  (the vertical separation of the second layer of antimony dimers from the bulk gallium atoms) were fitted to achieve the optimum agreement with the experimental reflectivity. Analysis showed that the top Sb layer of dimers and the second layer of antimony dimers are only marginally displaced from their bulk positions.

# Chapter 7

# Summary and future work

# 7.1 The atomic structure of $CaF_2$ -MnF<sub>2</sub>-Si(111) superlattices

### 7.1.1 Summary

We present the first high-resolution, synchrotron based, x-ray diffraction study to determine the 3-dimensional structure of  $MnF_2$ -CaF<sub>2</sub> superlattice samples. In-plane and out-of-plane measurements were made of the mature, buried  $CaF_2$ -Si(111) interface, and the structure of  $MnF_2$  thin films within the superlattices. Our results demonstrate that the modified semi-kinematical ROD software can be used to successfully determine the structure of a complex superlattice. The number of arithmetical operations carried out by ROD scales as the first power of the number of atoms contained within the simulation (ROD essentially adds the complex-valued scattering factors of all the atoms within the simulation). Provided sufficient computational storage space and numerical precision is available, simulations containing of the order of a hundred thousand atoms (equivalent to several tens of thousands of atomic layers) could be modelled. The sensitivity and flexibility of the surface x-ray diffraction technique have also been discussed. We have determined the 3-D structure of the mature, buried  $CaF_2$ -Si(111) interface using xray diffraction reflectivity and CTR scans. We show that samples grown with a high temperature  $CaF_2$  buffer possess, initially a "short" type-B interface that converts on atmospheric exposure to the "long" type-B CaF<sub>2</sub>-Si(111) interface. Our model is consistent with previous models proposed by Lucas [27], Sokolov [36] and Harada [37]. We have observed a fluorite structural phase for the ultrathin  $MnF_2$  layers within the repeated superlattice unit, stabilised by MBE growth, as opposed to its bulk rutile structure.

### 7.1.2 Future work

In this work we have allowed non-uniformity within the superlattice structure by introducing extra or missing layers within the repeated unit, but have neglected the effects of roughness. Further improvement in the agreement between the calculated and measured x-ray scattering will be achieved by incorporating roughness effects at the  $CaF_2$ -Si(111) interface and within the repeated unit. At the interface between dissimilar materials, the abrupt change in electron density is smoothed to produce a continuous function. This process will broaden and reduce the superlattice peaks away from the central Bragg reflections. We observed that ultra-thin layers of  $MnF_2$  below the critical thickness of 5 ML adopt the fluorite structure. A sample containing 5 ML was shown to have a slightly larger average interlayer spacing, indicating the onset of a structural transition. Further measurement of samples containing thicker MnF<sub>2</sub> layers (5–10 ML), is required to fully characterise the fluorite-rutile structural transition. We have obtained a detailed description of the  $CaF_2$ -Si(111) interface structure contained within superlattice structures. In all measurements, we observed the "long" type-B interface structure. It is known that type-A interface structures can be converted to the type-B interface with careful annealing. In-situ measurement of this process, using synchrotron x-ray diffraction, would help to explain the conversion mechanism. A fundamental understanding of the  $CaF_2$ -Si(111) interface structure will aid the future development of electronic devices based upon  $CaF_2$  technology.

## 7.2 The growth of Tl on $InSb(001)-c(4\times 4)$

### 7.2.1 Summary

### Formation of the InSb(001)-c(4×4) surface reconstruction

A prerequisite for the growth of  $In_{1-x}Tl_xSb$  on the  $InSb(001)-c(4\times 4)$  surface reconstruction is the growth of Tl on InSb. This aids the understanding of the atomic interactions between Tl and Sb and the preferred formation of Tl-Sb based compounds. The necessary starting point for the growth of Tl on InSb is the formation of a well ordered  $InSb(001)-c(4\times 4)$  surface reconstruction. We have developed Ar<sup>+</sup> ion bombardment and annealing cleaning techniques to produce atomically clean, well formed  $InSb-c(4\times 4)$ reconstructions using Sb capped and uncapped wafers. The presence of symmetric, in-plane x-ray diffraction peaks, produced by the hexagonal  $(0 \ 0 \ 3)$  and  $(0 \ 1 \ 2)$  Sb planes, indicated no preferential alignment for the amorphous antimony capping layer with respect to the substrate. A substantial re-ordering of the Sb cap was observed at 180°C during low temperature annealing by monitoring the intensity of the  $(1.47\ 0\ 0.1)$  in-plane amorphous Sb peak. At this temperature, the antimony atoms have increased mobility and neighbouring Sb crystallites are aligned. The protective capping layer was thermally desorbed by rapid annealing at 290°C under an antimony overpressure. Auger electron spectroscopy measurements showed that 1000Å thick antimony capping layers, grown at 200°C, were sufficient to prevent oxidation of the substrate for periods of atmospheric exposure of up to a year. Several annealing cycles under an antimony overpressure were required to form a well ordered  $InSb(001)-c(4\times 4)$  surface reconstruction. Surface prepared in this manner had atomic cleanliness and surface ordering (measured using in-plane xray diffraction scans) superior to that of an uncapped surface prepared using  $Ar^+$  ion bombardment and thermal annealing.

### The growth of Tl on InSb(001)-c(4×4)

We report a real-time, in-situ, study, using in-plane and out-of-plane (reflectivity) x-ray diffraction and AES measurements, to characterise the structure of Tl deposited using MBE (from a Knudsen source) on the InSb- $c(4 \times 4)$  reconstruction. The InSb anti-phase x-ray position was monitored throughout the growth. The lack of well formed oscillations in the room temperature growth curve after the formation of the first thallium layer indicates completion of a wetting layer followed by disordered 3-D island growth (Stranski-Krastanow (SK) mode) rather than well ordered layer-by-layer Frank-van der Merwe (FM) growth. A calculation in which the thallium atoms initially form a new layer above the top, partially filled (0.75 ML) Sb layer fitted the initial decrease in the experimentally measured anti-phase intensity. In contrast, calculations modelling the completion of the top partially occupied Sb layer before the formation of a new Tl layer produced an initial increase in intensity. The spacing between the top Sb layer and the first Tl layer and the Tl interplanar spacing was found to be consistent with the bulk thallium interplanar spacing of 2.7625Å. The theoretical deposition rate was matched to the experimental completion rate of 1 ML in approximately 40 minutes. A specular reflectivity ridge after Tl deposition showed reflections produced by the  $(1 \ 0 \ 0)$ ,  $(0 \ 0 \ 2)$  and  $(1 \ 0 \ 1)$  planes of Tl and an additional Tl<sub>2</sub>O peak. In-plane x-ray diffraction peaks at h = 1.66 and k =1.634 can be attributed to either the  $(0\ 0\ 2)$  thallium planes (h=k=1.652), the  $(1\ 1$ 0) TlSb planes (h = k = 1.672) or the (3 3 0) planes of Tl<sub>7</sub>Sb<sub>2</sub> (h = k = 1.667). A peak at k = 1.721 can be attributed to the  $(1 \ 0 \ 1)$  plane of Tl. The lack of a  $(1 \ 0 \ 1)$  Tl peak in the h direction shows a preferential alignment of the Tl domains. The levels of oxygen and carbon based contamination of the Sb rich surface reconstruction, the Tl-Sb interface region and the Tl film were below the detectable limit of AES.

### 7.2.2 Future work

Reflectivity and in-plane measurements of submonolayer coverages of Tl on InSb would be sensitive to the structure of the Tl layers. The interlayer spacing between the first layer of Tl and the top Sb layer could be used to determine if the Tl-Sb bonds at the Tl / InSb interface are in either the TlSb or Tl<sub>7</sub>Sb<sub>2</sub> configuration. Investigating the different growth modes could also be achieved by depositing thallium at a range of substrate temperatures. LUXC is equipped to cool or heat the substrate over a wide temperature range (liquid nitrogen temperatures right up to 425°C where deposited Tl is evaporated from the sample surface) during growth. Further investigation is also required to determine the preferred formation of either the cubic TlSb structure or the complex cubic Tl<sub>7</sub>Sb<sub>2</sub> structure during co-deposition of Tl and Sb onto the InSb-c(4×4) reconstruction. Reflectivity measurements could be used to determine the out-of-plane lattice spacings for layer-by-layer growth of the Tl-Sb compound. In-plane x-ray powder diffraction peaks would indicate the formation of identifiable amorphous compounds. This will help to indicate if In<sub>1-x</sub>Tl<sub>x</sub>Sb layers with the zincblende structure can be stabilised using MBE growth.

# 7.3 The atomic structure of the $GaSb(001)-c(2\times 6)$ surface reconstruction

### 7.3.1 Summary

We have developed cleaning procedures for antimony capped and uncapped GaSb samples using  $Ar^+$  ion bombardment and thermal annealing to produce well ordered, atomically clean GaSb(001)-c(2×6) surface reconstructions. Using AES measurements we showed heating uncapped samples to approximately 495°C, under an antimony overpressure, was sufficient to remove the oxygen component of the surface contamination. However, higher temperature anneals were insufficient to remove the carbon contamination. For antimony capped samples, we showed that a 1000Å Sb cap is sufficient to protect the MBE grown GaSb buffer layer from oxidation during atmospheric exposure for periods of up to a year. Long, low temperature sample anneals have been shown to compromise the Sb cap and oxidise the substrate. This problem was solved by transferring samples, via the sample transfer port, after bake-out of the UHV chamber. Prior to decapping, two twenty minute bombardment cycles of 900eV Ar<sup>+</sup> ions (1–2  $\mu$ A beam current) were sufficient to remove the majority of the carbon and oxygen based surface contamination. It was noted that longer periods of sputtering are required to remove the surface contamination from GaSb compared to InSb. The presence of symmetric, in-plane x-ray diffraction peaks, produced by the hexagonal  $(0\ 1\ 2)$  and  $(0\ 2\ 4)$  Sb planes, indicated no preferential alignment for the amorphous antimony capping layer with respect to the substrate. Analogous to antimony capped InSb, a substantial re-ordering of the Sb cap was observed at 180°C during low temperature heating. Full desorption of the cap was achieved by rapidly heating the sample and annealing at 310°C under an Sb overpressure. The formation of a " $(1 \times 3)$ " surface reconstruction was observed by the appearance of intense third order peaks in the  $\mathbf{b}_2$  direction and weaker half order peaks in the  $\mathbf{b}_1$  direction. Measurement of third order peaks in a  $(0.5 \ k \ 0.3)$  scan conclusively showed the symmetry of the reconstruction to be  $c(2\times 6)$  rather than  $(2\times 3)$ . The reflectivity was measured to probe the out-of-plane structure of the reconstruction. Theoretical fits to the experimental data indicate that both the top and the second layer of antimony dimers lie close to their bulk positions.

### 7.3.2 Future work

There is a pressing need to investigate the metallic " $(1\times5)$ " reconstructions. The reported structures, measured using STM, violate the electron counting principle. Having developed methods to produce well ordered GaSb(001)-c(2×6) surface reconstructions, the next stage is to investigate the structural transition to the " $(1\times5)$ " reconstructions and perform a full structural x-ray analysis of the reconstructions formed.

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