The Epitaxial Growth and Structure of Metal Overlayers on Oriented Substrates Studied by Surface X-Ray Diffraction

Thesis submitted for the degree of Doctor of Philosophy at the University of Leicester

by

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Abstract

The growth mode and structure of metal overlayers, stabilised by molecular beam epitaxy, on oriented semiconductor and metal substrates, was investigated using surface x-ray diffraction and synchrotron radiation.

The growth of the metastable fcc phase of Fe on Cu(001) at 300 K followed a layer-by-layer mode with limited atomic intermixing of Fe and Cu at the overlayer-substrate interface. Relaxation to the bulk bcc Fe structure occurred at a critical coverage dependent on the growth conditions. Fe deposition at higher substrate temperatures was characterised by strong Fe-Cu intermixing giving poor layer development. The growth was diffusion limited at low temperature. The vertical morphology of clean Cu(001) and adsorbate-covered surfaces at specific Fe coverages was determined from kinematical analysis of intensity measurements perpendicular to the surface and showed changes in the surface interlayer spacing with film thickness.

The metastable bcc phase of Co grown on GaAs(001) evolved in a predominantly three-dimensional manner with significant disruption of the semiconductor substrate, causing inclusion of As and Ga into the growing metal film. The structure of the Co film, determined from x-ray specular reflectivity measurements, was consistent with bcc Co. The behaviour of Fe deposited on GaAs(001) was similar, although the overlayer formation was better ordered.

In deposited on the Si(001)2×1 surface at substrate temperatures between 300 to 623 K exhibited a Stranski-Krastanov growth mode, that is the formation of one or two atomic monolayers (ML), followed by three-dimensional island formation. The metal induced a series of coverage and temperature dependent surface reconstructions. Deposition of In at 300 K caused only minimal substrate disruption, whereas In and Ga interacted strongly with the dimerised Si(001)2×1 surface at a substrate temperature of 373 K. During formation of the Si(001)2×1-In surface reconstruction the dimerised Si structure was partly destroyed and replaced by In dimers.
Acknowledgements

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The experiments were carried out at the Synchrotron Radiation Source, Daresbury Laboratory, UK, and I would like to express my gratitude to all the staff for their assistance during experiments, especially Dr. Tracy Turner, the station master of station 9.4. I am indebted to Chris Jeynes and the University of Surrey for prompt and detailed RBS analysis of my samples.

Finally, very special thanks are due to my family and friends for all their support and encouragement during the course of my university studies.
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Chapter 1

Introduction

The bulk structure of crystals has been studied for many decades and the physical properties of common materials are well known. The physical characteristics are derived from the types of atoms contained in the crystal along with the position occupied by each atom in the lattice. Consequently, the termination of a bulk crystal by a surface can dramatically affect the physical properties of the material in a number of fundamental ways, inducing novel behaviour quite different from that of the bulk material. The reduction in co-ordination of the surface atoms can lead to relaxation and reconstruction of the atomic structure within the surface region (typically a depth of several atomic layers) as the atoms rearrange themselves in order to minimise the surface free energy.

The electronic structure at the crystal surface is closely related to the atomic order. Changes in one directly influence the other and, in consequence, affect the electronic and magnetic properties at the surface. A detailed knowledge of the atomic behaviour of a surface when in a state of equilibrium and non-equilibrium, for example, during epitaxial growth, is essential to an understanding of its chemical and magnetic properties. The ability to control the behaviour of a surface or thin film at an atomic level has opened up the possibility of the fabrication of structures with properties tailored to satisfy specific objectives.

Interest in the surfaces and interfaces of materials has steadily increased in recent years, encouraged by the development of many techniques for the growth of surfaces and interfaces, for example, molecular beam epitaxy (MBE) and metal organo-chemical vapour deposition (MOCVD). In combination with the ever more powerful techniques for the characterisation of surfaces available in the laboratory and at synchrotron radiation facilities, for example scanning tunnelling microscopy (STM), atom force microscopy (AFM) and surface x-ray diffraction (SXRD), the field of surface science is flourishing.

MBE may be used to grow layered crystal structures on oriented substrates and the process is common in the fabrication of electronic devices in industry. Metal films deposited on semiconductor substrates are the primary stage of fabrication in device manufacture and the basis of the electrical connections for such devices. The development of device fabrication using epitaxial growth is a direct consequence of advances made in surface science research. The link between
device performance and reliability and the structure of the surface or interface has become more apparent in recent years. The MBE process is influenced by many factors, including substrate cleanliness, substrate temperature, surface orientation, deposition rate, impurity concentration, UHV base pressure, and lattice mismatch, and the role of each needs to be understood.

The first vacuum deposited films were produced as early as 1936 by Bruck who deposited iron on the cleaved face of a sodium chloride crystal. In the last three decades major advancements have been made in the design of ultra-high vacuum (UHV) equipment, now making pressures of $10^{-10}$ Torr routinely attainable (Patrician et al 1971). In addition, parallel advancement in growth and surface analysis techniques allowed artificial materials to be stabilised in thin film form by epitaxial growth and investigated with many different analysis techniques. The advent of synchrotron radiation sources enabled state of the art experiments to be performed by providing high intensity, collimated, tuneable radiation sources. Accompanying the advances made in the experimental field over recent decades has been an enormous increase in available computing power, thus permitting theorists to carry out total energy calculations for a large variety of new structures in both two and three dimensions.

An important research area from a fundamental and industrial perspective is the growth of metal layers on oriented substrates. For example, metastable phases can be readily induced through epitaxial growth of metal films on metal and semiconductor substrates allowing the exploitation of the novel magnetic phases associated with these structures. Not only does this allow the study of certain metastable phases at room temperature, but application should be possible in the magnetic recording industry.

The growth and stabilisation of non-equilibrium structures may be realised through MBE onto suitable substrates and this affords the opportunity to exploit the many novel magnetic phases that are closely linked with the existence of the metastable phase and much technological interest is directed towards this area. The energy changes associated with the formation of a metastable structure are of the same order of magnitude as the changes that separate different magnetic phases in certain metals. Many different magnetic phases may have energy minima situated near the same lattice constant, for example, fcc Fe, and, in consequence, novel and interesting magnetic phenomena are induced through the formation of such metastable phases, including surface magnetism. It is important to fully understand the development of the film structure as a function of film thickness and relate the magnetic phenomena to the crystallographic character. Even subtle structural changes, such as a small
expansion in the interlayer spacing, can strongly affect the magnetic behaviour. Only then can a full interpretation of the magnetic phenomena be formulated.

A metastable structure may be a known phase of the bulk material which can be stabilised under conditions of temperature and pressure other than those normally associated with the naturally occurring state, or the metastable phase may not be present on the equilibrium phase diagram at all. An example of each type of metastable structure is $\text{fcc Fe}$, which appears on the bulk phase diagram at high temperature but can be stabilised by epitaxy on Cu(001) at room temperature (RT), and $\text{bcc Co}$, which does not appear on the Co equilibrium phase diagram, but may be stabilised on the (110) and (001) surfaces of GaAs at RT.

Epitaxy onto a suitable substrate forces the deposited film to adopt a novel atomic structure due to the overriding influence of the substrate lattice. In general, the lattice parameters of the overlayer and substrate are closely matched. Many processes occur during the epitaxial stabilisation of a metastable structure and there is a fine balance between the strain energy of the metastable structure and other competing energies. Upon reaching a certain film thickness, known as the critical thickness, the defect energy becomes sufficiently large to cause the structure to relax to an equilibrium bulk structure with a lattice constant near that of the growing film.

With the steadily increasing importance of micro- and nanotechnology and a general trend toward miniaturisation in electronic device fabrication, for example, quantum well and low dimensional structures generally, understanding the processes involved in the growth of metal-semiconductor interfaces on an atomic scale is of paramount importance. The structure that evolves in the initial stages of overlayer formation will determine any subsequent growth patterns. The film quality at the interface, that is, essentially the first monolayer or so, will principally determine the growth mode of the film. Fabrication of any electronic device requires the formation of an electrical contact between a metal and a semiconductor surface and the quality, integrity and structure of this interface will critically affect the device performance and reliability. The presence of defects and impurities, surface steps, etc. can influence the production procedure, reproducibility, and reliability of a device and the role of each needs to be understood. Although Si(001) is probably technologically the most important semiconductor surface, few experiments have studied the initial stages of growth on this surface. In part, this is due to the experimental difficulties associated with the preparation of high quality, clean Si(001) surfaces since the (001) face of silicon is a higher energy surface than the (111) face and therefore less stable against roughening.
In this thesis a study is made of the growth of metals on single crystal metal and semiconductor substrates principally using the technique of SXRD. Chapter 2 introduces the concept of the metastable phase of a metal, defining different phases that can exist and giving specific examples of metals that exhibit metastability. In chapter 3 the kinematical theory of x-ray diffraction is developed and applied to scattering from crystal surfaces. The theory of Auger electron spectroscopy (AES) is also outlined. Chapter 4 describes the experimental techniques and equipment used to study the surface structures described in this thesis, including the method of collecting and analysing the data. The ultra-high vacuum (UHV) environmental chamber used to prepare the substrate and adsorbate structures is described. The specifications of the x-ray beam line station 9.4 at Daresbury Laboratory are outlined, including a description of the optics and diffractometer.

In chapters 5 and 6 the growth and structure of metastable fcc Fe on Cu(001) studied as a function of Fe coverage and substrate temperature is described. By employing epitaxy the metastable fcc Fe phase evolved on the Cu(001) surface at 300 K in a layer-by-layer growth mode, before relaxing to the bulk bcc Fe phase at a coverage of about 13 monolayers (ML). An interchange of Fe and Cu atoms was initially observed at the overlayer-substrate interface. Growth at 373 K began with the formation of a bilayer, followed by single layers, however, epitaxial breakdown occurred soon afterwards. At a substrate temperature of 473 K the amount of atomic intermixing increased resulting in poor quality layer formation. Growth at 85 K was diffusion limited. An expansion of the interlayer spacing at the surface of the Fe film was observed as a function of film thickness and may be correlated to the unusual magnetic behaviour possessed by the films (Pescia et al 1987).

In chapter 7 the MBE growth of Co and Fe on the GaAs(001) surface is reported. The initial stages of growth of the metastable phase of Co were characterised by significant intermixing of the deposited atoms and the substrate species at the metal-semiconductor interface which caused inclusion of As and, to a lesser extent, Ga in the growing metal film. Segregation of As to the surface of the Co overlayer was also observed. The growth of Fe on GaAs(001) was found to be better ordered, although still following the same general pattern.

Chapter 8 reports on a study of the growth of In and Ga on the Si(001)2×1 surface. The latter system is especially relevant to current research objectives since particular interest lies with inducing epitaxial films of GaAs to form on Si. Indium overlayer growth obeyed a Stranaski-Krastanov mode at all substrate
temperatures, with three-dimensional island coalescence following the formation of one or two atomic monolayers, determined in real time from simultaneous AES and SXRD measurements during deposition. The growth of Ga was more disordered. The additional sensitivity of x-ray scattering to overlayer growth was apparent. XRD measurements of fractional order diffraction peaks from the Si(001)2×1 surface reconstruction indicated that the interaction of the In adatoms with the Si surface at 300 K was weak, with only slight disruption of the underlying Si reconstruction, whereas In and Ga adatoms strongly interacted with the Si dimer structure at 373 K. A complicated series of surface reconstructions were induced as a function of metal coverage, observed using low energy electron diffraction (LEED), based on metal ad-dimers. An investigation of the Si(001)2×1-In and Si(001)2×2-In reconstructions was made. The Si(001)2×1-In surface reconstruction consisted of In dimers at the surface rather than Si dimers and was quite disordered. The 2×2-In reconstruction, although observable using LEED, was too poorly ordered to be measured using x-ray diffraction.

Chapter 9 provides a summary of the work presented in this thesis and gives suggestions for further work.
Chapter 2

Metastability of 3d Metal Films

2.1 Summary

The work contained in this thesis includes a study of two transition metal metastable phases, fcc Fe and bcc Co. This chapter serves to introduce the concept of the metastable phase and highlight the interesting structural and magnetic properties associated with such phases. Fcc Fe (γ-Fe) is a true thermodynamically stable high temperature phase which can be formed at room temperature by molecular beam epitaxy (MBE) onto Cu(001). Bcc Co is a non-thermodynamic metastable phase, which does not appear on the equilibrium phase diagram of Co, but can be prepared in an identical manner by epitaxial growth on GaAs surfaces.

The study of metastable phases is a fruitful and active area of research allowing investigation into a wide variety of fundamental areas (Jin and Ketterson 1989, Koon et al 1987, Baibich et al 1988) and providing technological benefits (Palmstrom and Morgan 1985, Prinz 1990). A major part of this thesis is concerned with an investigation into the stabilisation of the metastable phases of magnetic 3d metals grown epitaxially on single crystal substrates. Elemental magnetic 3d metals are of particular interest because they exist in a variety of different crystallographic and magnetic phases. The magnetic properties of the deposited film often depend critically on the choice of substrate and the growth conditions (Hong et al 1989). Examples of the crystal structures that result when a given 3d metal is vapour deposited onto a particular substrate are presented in an experimental study of the growth and atomic structure of fcc γ-Fe on Cu(001) (Chapters 5 and 6), and bcc α-Co on GaAs(001) (Chapter 7).

2.2 Uniaxially-Strain-Distorted Structures

Figure 2.1 shows the equilibrium phase diagram of Fe (Takahashi and Basset 1964). At ambient pressure the ferromagnetic α-Fe (bcc) phase exists below 910°C, the anti-ferromagnetic γ-Fe (fcc) phase occurs up to 1390°C, after which the non-magnetic δ-Fe phase persists until the melting point of Fe is reached at 1534°C. The phase diagram is established for bulk Fe under hydrostatic pressure, a situation which is quite different from that of epitaxial growth. In epitaxial growth the only force exerted on the metal film is due to the overlayer-substrate
Figure 2.1 Thermodynamic phase diagram of Fe (Takahashi and Basset 1964).
interfacial bonding, which can be either compressive or tensile, and drives the film into specific crystallographic structures. The metastable film will compensate for the in-plane constraints applied by the substrate surface unit cell by relaxing the interplanar spacing normal to the surface and the resulting tetragonally distorted structure will be stable if it is energetically close to a metastable phase, assuming there is not a bulk crystallographic phase whose total energy is a minimum at a lattice constant close to that defined by the interface.

Most metals will grow with a uniaxial strain distortion normal to the substrate surface as the unit cell attempts to minimise its energy by maintaining a volume close to its bulk value. The ultimate thickness (critical thickness) of a uniaxially distorted film depends on the energy balance between the energy associated with the bonding at the interface, the energy necessary to introduce strain relieving defects and the accumulated energy associated with the strain distortion. There is an energy per unit cell associated with its distortion away from the bulk minimum and every added layer contributes to this latter energy until it exceeds that necessary to create defects or break the interfacial bonds and the system relaxes to the bulk phase at the critical thickness.

### 2.3 Unstrained Metastable Structures

If the induced overlayer lattice parameter exactly matches that corresponding to a higher energy phase, for example, fcc γ-Fe and Cu(001), then an unstrained metastable phase will result and, in theory, the film will be perfectly cubic. Even so, the film is still limited to an ultimate thickness, since the accumulated energy of each unit cell is greater than that of the bulk bcc α-Fe unit cell, and the energy difference between the minima of the two phases increases until the structure relaxes to the lower energy one.

A crystal film can be grown under tensile stress via epitaxial growth on a suitable substrate to induce an expansion of the adsorbate lattice parameter. The growth of crystal structures in such a manner can result in the stabilisation of a uniaxially-strained film or a metastable phase, if one exists with a minimum energy near that corresponding to the expanded lattice constant of the film, for example, bcc Co on GaAs.
2.4 High Temperature Thermodynamic Phases

The lattice match between the substrate and overlayer may be sufficiently close that a stable or metastable three-dimensional phase may result. Table 2.1 (after Prinz, 1991) lists the most commonly studied overlayer-substrate systems for the thermodynamically stable phases of 3d magnetic metals. The thermodynamically stable high temperature fcc γ-Fe phase may be formed at low temperature by epitaxy on a single crystal copper substrate.

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<tr>
<th>Substrate Overlayer</th>
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<tr>
<td>Substrate (a_0, \text{Å})</td>
<td>Overlayer (a_0, \text{Å})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fcc Cu (3.61) fcc Ni (3.52)</td>
<td>β-Co (3.55) γ-Fe (3.59)</td>
<td></td>
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<tr>
<td>45° rotation on (001):</td>
<td></td>
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</tr>
<tr>
<td>fcc LiF (4.02) bcc α-Fe (2.867)</td>
<td></td>
<td></td>
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<tr>
<td>Al (4.05) × (\sqrt{2})</td>
<td></td>
<td></td>
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<tr>
<td>Au (4.07) = 4.055</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag (4.09) p((\frac{\sqrt{2}}{2}) × (\frac{\sqrt{2}}{2})) on (001):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fcc NaCl (5.64) bcc α-Fe (2.867)</td>
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<td></td>
</tr>
<tr>
<td>AlAs (5.62) × 2</td>
<td></td>
<td></td>
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<tr>
<td>GaAs (5.65) = 5.734</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge (5.66)</td>
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<tr>
<td>ZnSe (5.67)</td>
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Table 2.1 The most commonly studied film-substrate combinations for some of the thermodynamic stable phases of the 3d magnetic elements, after Prinz (1991).

2.4.1 fcc γ-Fe on Cu(001)

The fcc γ-Fe phase can be formed either by molecular beam epitaxy (MBE) onto a Cu(001) substrate, Fe precipitation in a copper matrix at room temperature, or at high temperature on the surface of Cu (Lu et al 1989). Extrapolation of the high temperature fcc lattice constant to room temperature yields a lattice constant of 3.59 Å for the fcc phase of Fe (Lu et al 1989) giving at 0.6% lattice mismatch with the Cu(001) surface. There is only a small energy difference between the bcc α-Fe and fcc γ-Fe phases and the strain energy resulting when Fe grows on Cu(001) is substantial, probably exceeding the difference between the two phases.
Figure 2.2 Binding Energy curves for fcc γ-Fe vs. cubic lattice constant $a$ in Å. Energy changes per atom in mRy referenced to the minimum (Moruzzi et al 1989).
Experimental work on γ-Fe dates back to 1956 (Hase), although reliable ultra-high vacuum (UHV) results were first produced in 1968 by Jesser and Matthews.

The fcc structure of Fe is of particular interest because many magnetic phases exist near the lattice constant of γ-Fe arising from competing magnetic structures (Figure 2.2, after Moruzzi et al 1989). This is a consequence of the change in the structural energy (~0.1 eV) being of the same magnitude as that associated with a change in the magnetic structure.

2.5 Non-thermodynamic metastable phases

2.5.1 The bcc Phase of Co

The fcc structure of Co is a naturally occurring ferromagnetic phase, whereas the bcc phase of Co does not appear on the known thermodynamic phase diagram. The metastable phase was not experimentally realised, although proposed by theoretical calculations (Ellis and Greiner 1941), until the advent of MBE allowed expanded-lattice films to be prepared. The existence of this phase of Co was predicted from investigation of the Fe-Co alloy phase diagram, which supports the bcc phase up to a concentration of 75% Co, as shown in Figure 2.3. The predicted lattice constant for bcc Co is 2.819 Å, which means that the bcc Co lattice can be stabilised on the GaAs surface with only a 0.4% mismatch with the GaAs lattice constant divided by two (2.825 Å).

Previous experimental measurements demonstrated that bcc Fe (2.867 Å) could be epitaxially grown on GaAs substrates (Waldrop and Grant 1979) and epitaxial Co films were successfully stabilised on GaAs surfaces (Prinz 1985). Bcc Co is now one of the most commonly studied 3d magnetic metastable phases. The bcc structure of Co was shown to exist at a coverage of 4 ML, when grown on the GaAs(001) surface (at 175°C), with no indication of tetragonal distortion perpendicular to the plane of growth (Jonker et al 1991). The bcc Co films were ferromagnetic (Prinz 1985), supporting total energy calculations which predicted ferromagnetism at the same lattice constant (Bagayoko et al 1983, Moruzzi et al 1986).
Figure 2.3  Lattice constant vs. composition for the bcc Fe-Co alloy system (after Ellis and Greiner 1941).
2.6 Growth of Metals on Semiconductor Substrates

Semiconductor substrates provide an attractive template for the epitaxial growth of metastable metal films. Ge, GaAs, AlAs and ZnSe substrates all have lattice constants of around 5.65 Å, which (divided by two) are close to the lattice constants of many 3d metals, for example, bcc Co (2.82 Å), and bcc Fe (2.87 Å). The successful epitaxial growth of bcc Co on GaAs, and Fe on GaAs, Ge, and ZnSe has been achieved.

2.7 Conclusions

It is obvious that metastable phases are of special interest due to their novel structural and magnetic properties. Research into the metastable phases of 3d magnetic metals stabilised on single crystal substrates is a growing field encompassing many overlayer-substrate combinations. Correlation of the metastable structure with the magnetic properties is paramount to a full understanding of the novel behaviour. Even so, certain aspects of metal on semiconductor growth are still not fully understood, for example, the exact chemistry at the overlayer-substrate interface and the dependence of the film properties on the growth conditions. Further investigations of such systems are required.
Chapter 3

Theory

3.1 Summary

X-ray diffraction (XRD) is widely used for the determination of the structure of materials on an atomic scale. The technique has been used for almost a century to characterise the bulk structure of crystals. Applying the technique to the study of the surfaces of crystals is a more recent development (Feidenhans'l 1989, Johnson 1991, Robinson and Tweet 1991, 1992). The weak scattering of x-rays with matter permits a simple kinematic (or single scattering) approximation to be applied to the analysis of the measured data allowing direct interpretation of the atomic geometry. The scattering from the surface region, which is typically a few atomic layers deep, is very weak and the study of surfaces by x-ray diffraction necessitates the use of high intensity x-ray sources, such as a rotating anode source, but more typically an electron synchrotron or storage ring. The large coherence length of synchrotron beams means that ordering on the length scale of greater than $10^3 \, \text{Å}$ can be monitored. XRD combined with synchrotron radiation is therefore well suited to the study of morphology of flat semiconductor surfaces.

In this chapter the theory of x-ray scattering from a crystal surface is developed. After describing the scattering from a single electron the theory is extended to encompass bulk and surface scattering from crystal structures, introducing the concepts of reciprocal space and crystal truncation rods (CTRs).

The theory of Auger electron spectroscopy (AES), an element specific probe for chemical surface analysis and monitoring adsorbate overlayer growth modes, is also outlined.

3.2 X-Ray Diffraction Theory

3.2.1 The Scattering of X-Rays by Atoms

X-ray diffraction measures the Fourier transform of the electron density. The Fourier transform of a two-dimensional object, such as a surface or interface, is a rod in reciprocal space. By measuring the intensity profile of the rod in reciprocal space, and comparing the measured profile with that calculated from a theoretical
model, it is possible to extract statistical information about the nature of the interface.

X-rays scatter weakly. In kinematical analysis the single scattering (or first Born) approximation is used, in which it is assumed that the diffracted wave is made up of contributions scattered directly from the incident wave, i.e. a result of a single scattering event without intermediate scattering from other atoms. A surface can be considered equivalent to a small crystal and therefore the amplitude of the scattered wave is much less than that of the incident wave and the total electric field may be replaced by the incoming wave field, \( E(r) \), in the formulation. In addition, it is assumed that the distance to the observation point is large compared with the dimensions of the scattering field. These conditions are satisfied in a typical surface x-ray diffraction (SXRD) experiment. Also, as we are interested only in elastic scattering, we need only consider a single wavelength of radiation.

Consider a plane wave, with amplitude \( E_0 \) and wave vector \( \mathbf{k}_i \), incident on an atom at position \( \mathbf{r} \). The incident beam is assumed to be a plane wave and its amplitude is given by (neglecting the time dependence of the wave):

\[
E_i(r) = E_0 e^{-i\mathbf{k}_i \cdot \mathbf{r}} \tag{3.1}
\]

where \( r \) is the magnitude of distance between the scatterer and detector.

For an electron at \( r \) the amplitude of the scattered wave, \( A_{\text{electron}} \), in terms of the incident wave amplitude, \( A_i \), can be described using the Thompson Formula (Warren 1969, Jackson 1975) as below:

\[
A_{\text{electron}}(\mathbf{q}, \mathbf{r}) \exp(-i\mathbf{k}_f \cdot \mathbf{r}) = A_i \frac{e^2}{mc^2 R} \exp(-i\mathbf{k}_i \cdot \mathbf{r})
\]

\[
i.e. ~ A_{\text{electron}} = A_i \frac{e^2}{mc^2 R} \exp(-i\mathbf{q} \cdot \mathbf{r}) \tag{3.2}
\]

where \( \mathbf{q} \) is the momentum transfer given by \( \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \) (defined in Figure 3.1),

\( e \) is the charge of an electron,

\( m \) is the mass of an electron, and

\( R \) is large compared with the dimensions of the scattering field.

Eq. (3.2) defines the scattering amplitude from an individual electron. The outgoing wave is spherical. The constant \( e^2/mc^2 \) is very small (\( 3 \times 10^{-15} \) m) and therefore the total scattering cross-section will be small making the kinematical approximation valid.
Figure 3.1 The scattering triangle which defines the momentum transfer. $k_i$ is the incident beam and $k_f$ the scattered beam. For elastic scattering, we define $|k_i| = |k_f| = |k| = 2\pi/\lambda$ (Eq. 3.3).
The momentum transfer is defined as the vector difference between the ingoing and outgoing wavevector. For elastic scattering:

\[ |\mathbf{k}_i| = |\mathbf{k}_f| = |\mathbf{k}| = \frac{2\pi}{\lambda} \]  

(3.3)

where \( \lambda \) is the wavelength of the x-ray radiation.

The momentum transfer relates the experimental scattering angle, \( 2\theta \), to the theoretical scattering amplitude (Eq. 3.2) through the following equation (Bragg’s law):

\[ |\mathbf{q}| = 2|\mathbf{k}| \sin \left( \frac{2\theta}{2} \right) \]  

(3.4)

The scattering from a single electron is described by Eq. (3.2). The atomic form factor \( f(q) \) is defined as the Fourier transform of the electron density of a single atom, such that:

\[ f(q) = \int \rho(r') e^{-i\mathbf{q} \cdot \mathbf{r}'} d\mathbf{r}' \]  

(3.5)

where \( \rho(r) \) is the electron density of the atom.

To describe the scattering of x-rays from an atom we simply sum the scattering from individual electrons using the kinematical approximation. Substituting Eq. (3.5) into Eq. (3.2):

\[ A_{\text{atom}} = A_0 \frac{\mu^2}{mc^2 R} \int \rho(r') e^{-i\mathbf{q} \cdot \mathbf{r}'} d\mathbf{r}' \]  

(3.6)

where \( \mathbf{r}_j \) is the position of the jth atom with respect to the unit cell, and 
\[ \mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3. \]

Eq. (3.6) defines the scattering amplitude of a single atom in the unit cell. The sum of the atoms within the unit cell is given by:

\[ A_{\text{unit cell}} = A_0 \frac{\mu^2}{mc^2 R} F(q) e^{-i\mathbf{q} \cdot \mathbf{R}_n} \]  

(3.7)
where \( F(q) = \sum_j f_j(q) e^{-i\mathbf{q} \cdot \mathbf{r}_j} = \int \rho_n(r) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} \) (3.8)

where \( \rho_n(r) \) is the electron density in one unit cell centred at \( r = r_j \).

The Structure Factor, \( F(q) \), is defined as the sum of contributions to the scattering from individual atoms within one unit cell evaluated at the reciprocal lattice point \( (hkl) \). The atoms in the unit are assigned individual form factors, \( f_j(q) \), to account for different chemical elements. The structure factor is the Fourier transform of the electron density within the unit cell and it is assumed to be the summation of the electron densities of the individual atoms. Unlike the form factor, the structure factor is dependent on the direction of \( \mathbf{q} \) as well as the magnitude. The structure factor is therefore sensitive to the relative positions of the atoms in space. The next step is to describe the x-ray scattering in three dimensions (3D).

3.2.2 X-Ray Scattering by a 3D Crystal

The unit cells are now summed to make a whole crystal. Scattering becomes strongly focused along certain directions and produces the phenomenon known as diffraction. The atoms in a crystal lattice are arranged in a periodic array. Consider the atoms in an infinite three-dimensional crystal lattice, defined by the (orthogonal) vectors \( \mathbf{a}_1, \mathbf{a}_2 \), and \( \mathbf{a}_3 \). The position of an atom is given by \( \mathbf{R}_n + \mathbf{r}_j \). The total scattering amplitude is the sum of scattering amplitude for one unit cell repeated at all possible lattice vectors. So, if each atom scatters with its own amplitude and phase the total scattered wave will be the vector sum of the individual components. The phase factors are added up for the positions of the origin of the unit cell:

\[
A_{\text{crystal}} = A_0 \frac{e^2}{mc^2 \mathbf{R}} F(q) \sum_n e^{-i\mathbf{q} \cdot (n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3)}
\] (3.9)

where \( \mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \) (3.10)

is a lattice vector, with \( n_i \) an integer.

It can be shown that the diffracted intensity is the product of three orthogonal, periodic 6-function arrays and, in consequence, three separate conditions have to be simultaneously satisfied to give an intensity maximum:
\[ a_1, q = 2\pi h \]
\[ a_2, q = 2\pi k \]
\[ a_3, q = 2\pi l \]  
\[ (3.11) \]

where \( h, k, \) and \( l \) are Miller indices.

These are the Laue Conditions from which the positions of the Bragg peaks can be found. Sharp Bragg peaks are generated at integer order values of Miller indices. We define the reciprocal lattice parameters, \( b_i \), by:

\[ a_i, b_j = 2\pi \delta_{ij} \]  
\[ (3.12) \]

\[ \text{with } q = h b_1 + k b_2 + l b_3 \]  
\[ (3.13) \]

where \( \delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases} \)

Eq. (3.13) satisfies the conditions dictated by Eq. (3.11).

The scattering from a three dimensional crystal has been derived. Non-zero diffracted intensity is observed at discrete points in reciprocal space. The intensity at a point \((hkl)\) is given by:

\[ I_{bd} = \left| A_0 \frac{e^{2}}{mc^2R} F(h b_1 + k b_2 + l b_3) N_1 N_2 N_3 \right|^2 \]  
\[ (3.14) \]

where \( N_1, N_2, \) and \( N_3 \) are unit cells along the crystal axes.

### 3.2.3 Surface Diffraction

In the previous section we described the scattering amplitude from a bulk crystal. A real crystal is not infinite in three-dimensions and the effect of truncation by a surface must be considered. Atoms at the surface may be of a different element to the bulk lattice. Atoms in the surface region are in a very different environment to the atoms in the bulk of the crystal since the co-ordination of surface atoms is reduced, and changes in atomic structure can be expected. The surface atoms will rearrange, for example, by relaxation or reconstruction, in order to achieve a minimum in the surface free energy. Relaxation describes the movement of the plane as a whole perpendicular to the surface. Reconstruction is the individual movement of atoms, typically in-plane, to create a new (larger) periodicity in the
surface plane. We may therefore consider a real crystal to be made up of a bulk part, which is a perfect semi-infinite crystal truncated by a flat surface (i.e. bulk terminated), and a surface part where relaxation and reconstruction of the first few layers is significant. The crystal is semi-infinite in one direction and infinite in the other two directions. The scattering amplitude for a real crystal is determined from adding the scattering amplitudes independently calculated for the surface and bulk parts.

Scattering from the Surface Region

Only two of the conditions defined in Eq. (3.11) need be applied and the Laue condition for the direction perpendicular to the surface may be relaxed and may take any real value. Constructive interference may now occur at non-integer values of the perpendicular momentum transfer producing streaks of intensity perpendicular to the surface that connect each allowed bulk diffraction peak. This gives rise to rods of scattering which are extended in the direction perpendicular to the surface whilst remaining sharp in the other two directions. This is known as a crystal truncation rod (CTR) and arises simply from the truncation of a perfect crystal without relaxation or reconstruction (Robinson 1986). CTRs are orthogonal to the macroscopic surface (or interface), not to the crystallographic planes. Experimentally, one measures the intensity of the CTR as a function of perpendicular momentum transfer.

For a reconstructed surface, where the periodicity in the plane of the surface is an integer multiple of the substrate periodicity i.e. (mn), there will be scattering at positions in the reciprocal lattice where bulk scattering is forbidden, known as fractional order positions (Figure 3.2). A reconstructed surface will consist of many reconstructed domains with domain boundaries which cause width broadening of the fractional order rods (Vlieg et al 1989). For a random distribution of domain sizes the transverse profile of a fractional order rod will be Lorentzian with a full-width-at-half-maximum (FWHM) given by:

\[ q = \frac{2}{L} \]  

(3.15)

where \( L \) is the average domain size.

Bulk Scattering

In the plane of the surface the Laue conditions confine the scattering to sharp diffraction rods. As demonstrated by Robinson (1986) the rod profile in a direction perpendicular to the surface can be calculated by summing the scattered
amplitude from each layer, taking into account the appropriate phase factors and corrections for attenuation of the beam.

The total scattered amplitude is given by:

\[ A_{hk}^{\text{bulk}}(l) = F_{hk}(l) + F_{hk}(l)e^{-2\pi il}e^{ia_3}/\mu + F_{hk}(l)e^{-2\pi il2}e^{(2a_3)/\mu} + \cdots \quad (3.16) \]

\[ = F_{hk}(l) \sum_{n=0}^{\infty} e^{-2\pi n il} e^{-n a_3/\mu} \quad (3.17) \]

where \( \mu \) is the penetration depth, and \( a_3 \) is the periodic spacing of the planes perpendicular to the surface.

The attenuation term makes the series convergent and allows us to evaluate the summation using the standard result for a geometric progression:

\[ A_{hk}^{\text{bulk}}(l) = F_{hk}(l) \frac{1}{1 - e^{-2\pi il} e^{-a_3/\mu}} \quad (3.18) \]

if \( \mu >> a_3 \) then

\[ A_{hk}^{\text{bulk}}(l) = F_{hk}(l) \frac{1}{1 - e^{-2\pi il}} \]

\[ = F_{hk}(l) \frac{e^{il}}{2\sin \ell} \quad (3.19) \]

The amplitude of the CTR varies as a function of perpendicular momentum transfer. There is a phase change of \( \pi \) at \( \ell=1, 2, \) etc.

At integer values of \( \ell \), which coincide with the position of Bragg peaks for an infinite bulk crystal, the CTR scattering diverges, accompanied by a phase change of \( \pi \). In between the Bragg peaks the scattering is non-zero and halfway between two Bragg points, known as the anti-Bragg position, the scattering amplitude from the surface is equivalent to 0.5 monolayers of atoms. The anti-Bragg position offers maximum sensitivity to the formation of monolayer height islands at the surface (Vlieg et al 1989).

**Combined Bulk and Surface Scattering**

Within the kinematical approximation, the total scattered amplitude can be calculated by simply summing the bulk and surface contributions, taking account of appropriate phase terms, illustrated schematically in Figure 3.3. Therefore:
Figure 3.2 Schematic diagram of reciprocal space showing the rods of scattering.
Figure 3.3  Schematic diagram showing the interference of bulk and surface scattering contributions.
At fractional order positions in reciprocal space the scattering is purely due to the contribution from the surface, i.e. no bulk contribution. At integer order positions there is interference between the scattering amplitudes from the surface and bulk CTRs. The scattering from the surface region, which is only a few atomic layers in depth, will be limited and therefore the total scattering near (bulk) Bragg peaks will be dominated by the bulk contribution. Near the anti-Bragg position, however, the amplitude of the scattering from the surface will be of the same order of magnitude as that from the bulk and, in consequence, interference effects can be observed as a result of structural changes at the surface. These effects are sensitive to the choice of substrate and adsorbate materials.

A crucial result is that the interference effects between the bulk and surface CTR scattering is extremely sensitive to the structure of the surface. The amplitude and phase of the bulk scattering are well defined and the interference effects can be used to determine the surface structure to a high degree of precision and many examples of structure determination using SXRD are reported (Silfhout et al. 1990, Takahashi and Nakatani 1993).

In the above formulation the electrons in the crystal were assumed to be free, however, in a real crystal the electrons are bound. This assumption will only create problems if the x-ray frequency is near that of a resonant frequency of the electrons.

The Effect of Temperature on the Diffraction of X-Rays

The Debye-Waller Factor

In a real crystal (at a temperature greater than 0 K) the atoms do not occupy a definite position and they will vibrate about an average position. Even at room temperature the instantaneous atomic displacements may be appreciable as a result of thermal vibrations in the crystal. The effect of temperature on the diffraction peaks is described by a factor \( e^{-2M} \), the Debye-Waller factor. The reduction in intensity becomes greater as the temperature increases. The thermal diffuse scattering manifests itself as a background in reciprocal space and reduces the intensity of the measured diffraction peaks. The Debye-Waller factor is used to associate thermal fluctuation in the crystal with the scattering factor and can be described in the structure factor as follows:
\[ F_{\text{hel}} = \sum_j f_j e^{-\left(\frac{B_j r_j^2}{16\pi^2}\right)} e^{-2\pi i(hx_j + by_j + cz_j)} \]  

(3.21)

where \( B \) is the Debye-Waller parameter, and \( r_j \) is written in reduced coordinates \( (r_j = x_j a_1 + y_j a_2 + z_j a_3) \).

In this case the Debye-Waller parameter is assumed to be isotropic and can be related to the mean-square thermal vibration amplitude \( \langle u^2 \rangle \) using:

\[ B = 8\pi^2 \langle u^2 \rangle. \]  

(3.22)

Further information can be found in Pendry (1974), Warren (1969), and Jackson (1965).

### 3.2.4 Symmetry and Surface X-Ray Diffraction

When performing structure determinations using SXRD the symmetry of the measurements must be considered. The symmetry of bulk crystals is considered by Burns and Glazer (1992), and Hahn (1983, 1987). A point symmetry operation is specified with respect to a point which does not move during an operation, for example, rotation and reflection. Sets of symmetry elements which are self-consistent and complete are known as point groups. In a crystal the symmetry of the unit cell is called the space group and is a combination of the point group symmetry and translational symmetry. There are 17 possible two-dimensional (2D) space groups.

A reconstructed surface may exhibit a lower symmetry than the 2D point group of the bulk as a result of mirror planes or axes of rotation which may or may not be present in the reconstruction. Different domains, between which the atomic structure is related by rotation or reflection, may exist in similar proportions since they are equally energetically favourable, for example, the Si(111)4×1-In reconstruction has 3 domains rotated by 60° with respect to each other, and the Si(001)2×1 surface has two domains rotated by 90°.

#### The Effect of Symmetry on the Structure Factor

Let us consider the effect of symmetry on the SXRD measurements. The symmetry of the surface can be defined in general by:

\[ \rho(x) = \rho(\pi) \]  

(3.23)
where the operator \( \tau \) represents a rotation or reflection of the co-ordinate \( r \). The electron density is left unchanged by the symmetry operation, and therefore so is the crystal structure. The Structure Factor has been defined as the Fourier transform of the electron density of the unit cell (Eq. 3.8):

\[
F(q) = \int_{\text{unit cell}} \rho(r) e^{-iqr} dr
\]  

(3.24)

So, by substituting equation (3.23) and changing the order of integration:

\[
F(q) = \int_{\text{unit cell}} \rho(\tau) e^{-iqr'} d\tau
\]  

(3.25)

\[
F(\tau q) = \int_{\text{unit cell}} \rho(r) e^{-iqr'} dr
\]  

(3.26)

\[
\therefore F(q) = F(q\tau)
\]  

(3.27)

We therefore conclude that the diffraction data have the same point symmetry as the real space structure.

### 3.2.5 The Patterson Function

Model-independent information can be derived from the measured x-ray diffraction data by means of the Patterson function, which gives a picture of the structure without assumption of any model. It is defined as the auto-correlation function of the electron density in three-dimensions:

\[
P(r) = \int \rho(r) \rho(r-r') dr'
\]  

(3.28)

It is not possible to experimentally measure the electron density directly because only the amplitude of the structure factor can be recorded, not the phase (known as the phase problem). The Patterson function is common in x-ray crystallography and is related to the structure factor. A peak in the Patterson function represents an interatomic vector in the real crystal lattice. It can be shown, by taking the inverse Fourier transform of Eq. (3.8), that \( P(r) \) for 2D space is:
For a periodic surface, $F(q)$ is confined to discrete Bragg rods and the projection of the electron density onto the surface plane is given by:

$$
\rho(x, y) = \sum_{h,k,l=0} |F_{hkl}| e^{i(hx+ky)}
$$

(3.30)

Hence, the corresponding 2D pattern can be defined as (Warren 1990):

$$
\rho(x, y) = \sum_{h,k} F_{h}^{2}\cos(hx+ky)
$$

(3.31)

This is easily computed from measured structure factors and a positive peak represents an interatomic vector projected onto the surface plane. A true Patterson function is a sum over all $h$ and $k$, but only a limited data set is experimentally measurable. $P(r)$ is therefore calculated using fractional order reflections only to avoid complications derived from the bulk scattering contributions. Even so, information can be gained about the interatomic vectors from the experimentally determined Patterson function (Feidenhans'l 1989, Bohr et al 1985, 1986).

The Critical Angle

The critical angle for total external reflection, $\beta_c$, is defined, ignoring absorption effects, as (James 1982):

$$
\cos \beta_c = n
$$

(3.32)

where $n$ is the refractive index of the material.

For small angles:

$$
\beta_c = \sqrt{2\delta}
$$

(3.33)

where

$$
\delta = \frac{N\varepsilon_o^2\lambda^2}{2e_nmc^2}Z
$$

(3.34)

where $N$ is the number of atoms per unit volume = $\rho/A$

$Z$ is the atomic number of the atom,

$A$ is the atomic weight of the atom,

$\varepsilon_o$ is the permittivity of free space, and

$\rho$ the mass density of the solid (g cm$^{-3}$).
by substitution and using $\omega = 2\pi c/\lambda$:

$$\beta_c = \frac{\lambda e}{2\pi e} \left( \frac{1}{\epsilon_p} \right) \left( \frac{1}{z A} \right)^{1/2}$$

(3.35)

$$\therefore \beta_c = 0.133 \left( \frac{\rho Z}{A} \right)^{1/2} \lambda$$

(3.36)

The units of $\beta_c$ are degrees.

We can introduce a complex refractive index to account for absorption effects:

$$n = 1 - \delta - i\gamma$$

(3.37)

where

$$\gamma = \frac{\lambda \mu}{4\pi}$$

(3.38)

where $\mu$ is the absorption coefficient for the surface.

If the scattering angle, $\alpha$, is, for example, fixed at 2° then the specular peak corresponds to the incident grazing angle $\beta$ and the exit grazing angle $\beta'$ both being equal to 1°.

The diffuse wings around the specular peak are a consequence of the incident and exit angles independently being equal to the critical angle of the material, for example, for GaAs $\beta_c$ is 0.18° at $\lambda = 0.9$ Å, enhancing sensitivity to the surface roughness. The origin of the side peaks comes from the fact that whenever the critical angle is satisfied the x-ray field in the surface plane reaches a maximum, enhancing the coupling to the surface disorder. The scattering intensity of x-rays from disordered surfaces (Vlieg et al 1989) can be separated into a sharp 'Bragg' component and a broader 'diffuse' term related to the height-height correlation function or surface roughness. For total external reflection dynamical theory predicts additional peaks in the rocking curve (Sinha et al 1988).

### 3.3 Auger Electron Spectroscopy (AES)

The process was first discovered in 1925 (Auger 1925) and named after its discoverer. Landers (1953) later showed that it was possible to detect this secondary electron emission from surfaces under electron bombardment, after
Figure 3.4  (a) Schematic diagram of the Auger and x-ray fluorescence processes, (b) the Auger electrons appear as peaks on a strong secondary background. The Auger process is non-radiative.
which Harris (1968) electronically differentiated the detected signal with respect to energy to remove the secondary background and enhance the Auger signal. The technique is primarily used for surface chemical analysis but can also be used as a method for determining the growth mode of vapour deposited overlayers.

3.3.1 The Auger Process

The Auger process essentially occurs in two stages. Initially, an incident electron (or photon) with an energy of ~2.5 keV causes ionisation of a core level in an atom situated near or at the surface. An electron from a higher energy level fills this core hole and dissipates energy either by emission of a secondary (Auger) electron or a photon. The relative electron or photon yield depends on the initial core hole energy, with the photon yield dominating for energies typically of 10 keV. Figure 3.4 schematically illustrates the Auger process. The Auger electrons have well-defined energies that are characteristically linked to the emitting atom and this enables surface chemical analysis to be performed.

The nomenclature to describe the Auger process is $W_pX_qY_r$, where standard x-ray notation is used (K, L, M, N, etc.) to identify the initial ionised state ($W$), the level from which the core hole is filled ($X$), and the level from which the Auger electron is emitted ($Y$). The relevant quantum numbers for $W$, $X$, $Y$ are represented by $p$, $q$, and $r$, for example, $L_{1}=2S$, $L_{2}=2p_{1/2}$. Following the initial ionisation event, a redistribution of charge will occur which will affect all energy levels. It is difficult to compute the expected Auger energies with great certainty, but a reasonable estimate may be made using (Chung and Jenkins 1970):

$$KE = E_{W}^{Z} - \frac{1}{2}(E_{X}^{Z} + E_{Y}^{Z+1}) - \frac{1}{2}(E_{Y}^{Z} + E_{Y}^{Z+1})$$ (3.39)

where $Z$ is the atomic number of the emitting atom.

3.3.2 Overlayer Growth Monitored with AES

It is well known that vapour deposited films develop in distinct growth modes. Figure 3.5 illustrates the growth modes along with the expected Auger and x-ray signals as a function of deposition time. The process of monitoring the Auger signal with time is known as AST (Argile and Rhead 1989). The growth modes are defined as follows:

(a) Volmer-Weber mode (Volmer and Weber 1926): this is essentially a 3D growth behaviour, indicative of high lattice mismatch, and a reluctance to wet
the substrate surface. The AST decays exponentially and the x-ray curve intensity rapidly drops off.

(b) Frank van der Merwe mode (Frank and Merwe 1949a, b) : the completion of successive single atomic layers is characterised by evenly spaced linear breaks (in time) in the Auger curve and well-defined parabolas in the x-ray curve.

(c) Stranski-Krastanov mode (Stranski and Krastanov 1938) : After completion of one or two monolayers a 3D growth mode predominates. This is characterised by a single break in the AST plot followed by a roughly constant signal. The specular reflectivity shows a single parabolic oscillation up to a coverage of 1 ML, after which the signal gradually decays.

(d) step flow mode (van der Vegt 1995): during step flow the atomic layers grow outward from step edges along the terraces on the surface. The x-ray specular reflectivity remains unchanged by the advancing growth front, whereas the AST curves shows breaks similar to the Frank van der Merwe mode.

The above is a simplification of what happens in a real situation and other growth modes can be identified, such as simultaneous multilayer mode (SM), and monolayer plus simultaneous multilayer mode (MSM) (Rhead et al 1981), in which layers are built up at random, with the nth layer growing before completion of the (n-1)th layer, resulting in an exponential decay of the Auger signal.

Overlayer growth is affected by many factors, including substrate flatness, surface cleanliness, substrate temperature, vacuum conditions, evaporation rate, lattice mismatch and surface orientation. The growth mode can therefore be difficult to predict and monitoring the Auger signal with time is a simple starting point from which to approximately determine the overlayer growth mode. The AES method can also be used to calibrate overlayer thickness based on the heights of the measured Auger peaks for the overlayer and substrate (to an accuracy of \(\pm 2\%\)).
(a) 3D island growth mode (Volmer-Weber)

(b) 2D layer-by-layer growth mode (Frank van der Merwe)

(c) Stranski-Krastanov growth mode

(d) Step-flow growth mode

Figure 3.5  Schematic diagram illustrating the difference between the growth modes described in the text (a)-(d) and the associated AST and x-ray specular curves. The model describes the heteroepitaxy and assumes that the different atoms have the same atomic scattering factor and adopt the same crystal structure of the substrate.
Chapter 4

Experimental Techniques

4.1 Summary

The study of crystal structures by surface x-ray diffraction (SXRD) requires long periods of measurement on a single surface which must remain contamination free and this calls for an ultra high vacuum (UHV) environment. The UHV environmental chamber designed at Leicester University for in-situ SXRD measurements is described in this chapter. The chamber is fitted with surface science equipment for the preparation of substrates and overlayer structures. The growth of adsorbed species can be monitored in-situ using SXRD and Auger electron spectroscopy (AES) measurements in real time. The sample preparation procedures, ex-vacuo and in-situ, used to obtain atomically clean substrate surfaces are explained for silicon, copper and gallium arsenide.

The small scattering cross-sections inherent in x-ray diffraction measurements necessitates the use of high intensity x-ray sources, for example rotating anode and synchrotron sources. The surface diffraction apparatus at the synchrotron radiation source (SRS) at Daresbury Laboratory is outlined.

4.1.1 The Requirement for Ultra-High Vacuum

The study of atomically clean substrate and adsorbate surfaces is necessarily performed in an ultra-high vacuum (UHV) environment, i.e. a vacuum better than $10^{-9}$ mbar, in order to minimise sample surface contamination.

From kinetic theory (see, for example, Yarwood 1967) it can be shown that the number of monolayers $n$ of the residual atmosphere (with a mean molecular mass of 28 amu) forming on a surface at room temperature (RT) is given by:

$$n = 10^6 SP \text{ monolayers s}^{-1}$$  \hspace{1cm} (4.1)

where $S$ is the sticking coefficient, and  
$P$ is the gas pressure (in mbar).

In the case where $S=1$, every molecule that comes into contact with the surface will stick to it and one monolayer will form in approximately 1 hour at a pressure of $2\times10^{-10}$ mbar. The value of the sticking coefficient is strongly
dependent on the choice of adsorbate and substrate, as well as the substrate temperature. In this thesis a variety of different substrate and overlayer combinations are described and the time which the surface remains atomically clean (within the detection limits of AES) depends on the reactivity of the elements involved and the choice of substrate crystallographic face. A typical SXRD experiment may require over one hundred hours of measurements to record a sufficiently large data set and the need for an UHV environment is evident.

The techniques required to achieve UHV conditions are described in many textbooks (see, for example, Yarwood 1967, Redhead 1968).

4.2 Surface Science Techniques and Sample Preparation

4.2.1 The UHV Environmental Chamber

The x-ray diffraction measurements presented in this thesis were made using a UHV environmental chamber described by Norris et al (1987). Figure 4.1 schematically shows the environmental chamber coupled to the surface x-ray diffractometer. A photograph of the experimental set-up is shown in Plate 4.1.

The main chamber consists of a 8" diameter stainless steel tube with a number of side ports to accommodate various surface science equipment. Each port is directed towards the centre of the sample which is located at one end of the main tube. The surface science equipment includes a Vacuum Generators (VG) LEG31 electron gun with a VSW HAS0 hemispherical analyser for AES (see Sections 3.3 and 4.2.5), a VG argon ion bombardment gun for sputter cleaning of substrates, Knudsen cell vapour sources to allow UHV deposition of pure adsorbate materials (up to a six Knudsen sources may be simultaneously fitted on the chamber) and a VG SX200 residual gas analyser (RGA). The large flange opposite the sample can accommodate either a load-lock sample transfer/preparation chamber, or rear-view low energy electron diffraction (LEED) optics. The rear view LEED optics may be brought up to the sample surface using a linear drive mechanism (Taylor 1988). The substrate temperature is routinely monitored with an Ircon infra-red pyrometer; a thermocouple arrangement may be fitted to the sample heater close to the sample if required.

A large 200°×30° beryllium window, electron welded onto the wall of the main tube of the chamber, allows incident x-rays to enter the UHV chamber environment. The scattered x-rays exit the chamber through the same Be
Figure 4.1  Schematic diagram of the UHV environmental chamber used for SXRD measurements mounted on the x-ray diffractometer showing the out of plane detector assembly.
window and are collected by the detector. At UHV, the chamber is pumped by a Varian 400 l s\(^{-1}\) ion pump and a liquid nitrogen-cooled titanium sublimation pump (TSP). Gas handling, for example, during argon ion bombardment, is provided by a 400 l s\(^{-1}\) Balzers turbomolecular pump backed by a (fomblin oil) rotary pump. During gas handling operations the ion pump can be isolated from the main chamber using a manually operated gate valve.

When pumping down from atmospheric pressure a vane pump is used to achieve a vacuum of approximately 1 mbar, then liquid nitrogen-cooled adsorption pumps bring the pressure down to the range of operation of the turbomolecular pump (~10\(^{-5}\) mbar range). To reach UHV conditions the chamber is baked for 24 hours at about 423 K and thoroughly outgassed to routinely obtain a base pressure of 3\(\times\)10\(^{-11}\) mbar.

### 4.2.2 Sample Manipulation

The sample is mounted on the sample heater (Taylor et al 1991), as shown in Figure 4.2, which in turn is rigidly held in a differentially pumped rotary feedthrough. The sample surface is situated at the centre of the diffractometer circles (Section 4.4).

The rotary feedthrough, which was designed and constructed at Leicester University, is based on an earlier design (Fuoss 1984). Three viton sealing rings separate two differentially pumped sections allowing rotation of a highly-polished stainless steel tube through 360\(^\circ\) without leakage from the high vacuum stage to the UHV chamber, even at base pressures as low as 3\(\times\)10\(^{-11}\) mbar. Such rotation of the sample is essential in order to perform surface x-ray diffraction measurements (see Section 4.5). The low vacuum section (at 10\(^{-3}\) mbar) is pumped by a rotary pump and the high vacuum section (at 10\(^{-6}\) mbar) by a 50 l s\(^{-1}\) Balzers turbomolecular pump. The feedthrough is coupled to the UHV chamber by a bellows which allows ±15\(^\circ\) azimuthal rotation. In normal operation the rotary feedthrough is coupled to the φ axis of the diffractometer, as shown in Figure 4.2. During “off-line” operation the rotary feedthrough is clamped to the chamber with a bracket.

Figure 4.2 shows the assembly for holding the sample heater in the rotary feedthrough. The sample heater slides into the stainless steel tube at the end of the rotary feedthrough and is located, drawn-in and rigidly held by collets which grab a central square pin on the sample heater using a linear motion mechanism.
Plate 4.1  Photograph of the UHV environmental chamber used for SXRD measurements coupled to the x-ray diffractometer showing the out of plane detector assembly.
The linear motion is used to push or pull the collet thus releasing or holding the sample heater respectively.

The sample has dimensions 10×8×1.5 mm\(^3\) with steps cut in two opposite edges for clamping (see Figure 4.3). The sample surface therefore stands proud of the sample holder assembly allowing grazing incidence x-ray diffraction to be performed without shadowing from any sample heater components.

The sample holder and heater components are mounted off an alumina base plate, see Figure 4.2 (after Taylor et al 1991). The majority of the sample heater parts are made of either Mo or Ta in order to minimise contamination from the heater components when the heater is in operation. Four electrical connector pins are attached by Ta strips to four legs which support the top alumina plate. Two of the legs provide connections to the filament (0.2 mm thoriated W wire) which is surrounded by a Ta can. The other two legs are connected to the sample via D-plates, on which the sample is seated. The specially cut samples are firmly clamped by their stepped edges to the D-plates using Ta clips, which are in turn held in place by Mo screws. The whole assembly fits inside a stainless steel body which is screwed to an alumina base plate. Fixed to the centre of this base plate is the rectangular stainless steel clamping pin which locates into the collet of the sample holder, as described above.

The electrical power is supplied to the sample heater through the four pins on the back of the heater which fit into four sockets wired through the rotary feedthrough. Using combinations of the above electrical connections the sample can be radiatively heated to about 800 K with the filament alone, resistively heated to 1200 K and electron beam heated to 1600 K by applying a positive 1 kV potential to the sample in conjunction with the filament. Electron beam heating may also be achieved by applying a negative potential to the filament with the sample held at ground potential or a small positive potential. The sample temperature is monitored by a calibrated IR pyrometer through an IR UHV window (to within ±5 K), or a thermocouple attached to the sample heater close to the sample (to within ±20 K). An Ircon Modline Plus 6000 pyrometer is used in conjunction with neutral density filters to give reliable temperature measurement over 1300 K (Finney 1992). The sample heater design was modified, essentially by the removal of the alumina top plate, previously shown in Figure 4.2, to allow electron beam heating of Mo samples up to temperatures of 2300 K.

A load-lock sample transfer chamber is fitted to make efficient use of experimental beam time by allowing exchange of sample heaters and samples without breaking vacuum. The sample heater is unclamped by releasing the
Figure 4.2  Detailed schematic diagram of the sample heater and sample holder.
collet and picked up with a magnetic rotary/linear arm which locates three pegs into key-hole slots cut into the top ring of the sample heater. The whole sample heater assembly is removed from the main chamber through a gate valve into the sample transfer chamber (see Figure 4.2). A second sample heater may be introduced using the reverse procedure. Approximately three hours are needed to change samples.

During the course of the work described in this thesis sample transfer was only possible using the small transfer chamber, but a new load-lock sample preparation chamber has been designed and is available. The new preparation chamber incorporates a 400 l s⁻¹ Balzers turbomolecular pump and will allow surface preparation including sample heating (as described above), Ar ion bombardment, and oxygen cleaning, as well as UHV deposition prior to insertion of the sample into the main UHV chamber.

4.2.3 The Liquid Helium Cryostat

Modification of the sample holder design allows cooling of samples using liquid nitrogen or liquid helium. As with the original sample holder assembly there is the ability to exchange samples without breaking vacuum, but in addition the liquid helium cooled cryostat can be operated over a sample temperature range of 40 to 1300 K. The overall assembly of the sample holder, cryostat and rotary seal is shown in Figure 4.4. The design is based on the VG Cryoax HX Series and was built by Oxford Instruments, UK. The sample heater design is essentially the same as that previously shown in Figure 4.2, a small modification being the substitution of a copper central pin to improve heat conduction. Liquid He is supplied through separate flow and return pipes to enable cryogenic cooling and rotation of the cryostat with the diffractometer. The cryostat can be either run with liquid He or liquid nitrogen. When running the cryostat with liquid nitrogen the sample reached a temperature of 86 K after about 100 minutes, and achieved a temperature of 44 K after 180 minutes when liquid helium was the cryogen. Further details can be found elsewhere (Taylor and Norris 1994).

4.2.4 Knudsen Cell Vapour Sources

Metal was evaporated from a Knudsen effusion cell, illustrated in Figure 4.5 (Taylor & Newstead 1987). High purity material was used in each experiment, for example, Fe of purity 99.9998% (5N8). The evaporant material was placed in an alumina crucible, of 1 cm³ volume, around which was wound a 0.25 mm W wire filament. The crucible arrangement is contained inside in a hollow, stainless steel shroud through which water (or liquid nitrogen) is pumped in order to remove
Figure 4.4  Sample holder, liquid helium cryostat and rotary seal, mounted on the x-ray diffractometer and coupled to the UHV environmental chamber via bellows.
Plate 4.2  Photograph of liquid helium cryostat
(a) side view, and
(b) (following page) forward view showing the sample heater and sample in position.
radiated heat from the crucible. An alumina cap with a 3 mm hole in its end fits into the crucible and is held in place by the thermocouple arrangement giving a reliable estimate of the crucible temperature. The hole in the cap allows the vaporised metal to escape from the crucible, but prevents the evaporant falling out of the crucible when the vapour source is mounted pointing downwards on the UHV chamber. A shutter in front of the crucible, operated by a small rotary drive integral in the vapour cell design, controls exposure of the sample surface to the evaporant flux. The complete effusion cell is compact enough to fit on a single 70 mm conflat UHV flange.

The crucible is resistively heated using a Faraday TSV70 stabilised DC supply. The pressure can remain in the low $10^{-10}$ mbar range during evaporation provided that the effusion cell is thoroughly outgassed. A typical deposition rate of 1 monolayer (ML) in 12 minutes is used (i.e. 0.083 ML/minute), achieved using a power of about 80 Watts supplied to the filament for evaporation of Fe, where the cell temperature was approximately 1300 K. The temperature of the evaporator can be held at a desired value for prolonged periods, varying by only ±5 K. In the case of evaporation of pure In, a pyrolytic boron nitride (PBN) sleeve, containing 99.999% (5N) pure In wire, was fitted inside the standard alumina crucible. This prevents reaction of the In metal with the alumina crucible.

The above crucible and cap arrangement is perfectly adequate provided that the evaporant material is not molten at the evaporation temperature and can be fitted to either a downward or upward pointing port on the chamber. If this is not the case then the evaporant will leak from the crucible if the vapour source is mounted on a downward pointing port causing failure of the cell. A recent modification to the design allows all materials to be accommodated in a downward orientation, regardless of the melting temperature, giving full utilisation of all of the evaporator ports available on the UHV chamber (of which 2 point upwards and 4 point downwards). A Ta liner is inserted into the crucible, as illustrated in Figure 4.6, and secured using the thermocouple wires as previously and the molten evaporant is contained within it. The Ta liner is completely sealed apart from an offset hole at the front to allow the vaporised material to escape. The efficiency of the effusion cell is not significantly worsened by this modification and gives operating conditions only slightly different from those expected from the standard cell design. Spacer flanges need to be fitted on two specific chamber ports to allow operation of the linear drive mechanism for movement of the LEED optics past the effusion cells. The modified cell design has been successfully used to evaporate Pb, Tl, Ga, and In.
Figure 4.5 Schematic diagram of the Knudsen cell vapour source used for metal deposition with cryoshield sectioned.
Modification of the Knudsen cell crucible design (shown in Figure 4.5) by insertion of Ta liner inside the crucible to allow evaporation of low melting point materials in a downwards pointing orientation on the UHV chamber.
4.2.5 Auger Electron Spectroscopy

The Auger process is described theoretically in Section 3.3 and the experimental arrangement used for Auger electron spectroscopy (AES) is shown in Figure 4.7. The AES data was obtained in a differentiating mode using lock-in techniques and by applying a modulation voltage to the sample. The AES intensity is defined as the peak to peak height of the specified line.

A VG LEG31 electron gun emits electrons of energy 2.0 keV which are incident on the sample causing excitation of the atomic species in the surface region. The emitted Auger electrons are focused on to the entrance slit of a VSW HA50 hemispherical analyser by an electrostatic lens. Only electrons of a certain energy, known as the pass energy, will emerge from the hemispherical analyser and be detected by an electron multiplying channeltron. The analyser can be computer controlled through a CAMAC crate via a digital to analogue converter (DAC), or a PC. The amplified Auger yield is electronically differentiated by a phase-sensitive lock-in amplifier to remove the broad background signal. An example of a typical measured Auger spectrum is given in Figure 4.8.

Determination of Growth Modes Using As-t

The nature of the growth of adsorbed layers on a substrate formed by vapour deposition can be determined from a plot of the Auger signal against time (AST), see Figure 4.9. This is achieved in-situ by repeatedly scanning over a small energy range containing a single Auger peak, characteristic of the substrate or overlayer, during vapour deposition. By fitting a seventh order polynomial to the measured peak the height is calculated in real time and plotted. A special design feature of the UHV chamber allows this to be performed without disturbance of the sample or interruption of the vapour deposition and can be simultaneously monitored with the x-ray signal.

4.2.6 Sample Preparation

The silicon and copper samples used for SXRD experiments in this thesis were specially cut (at the Materials Centre at the University of Birmingham) with steps at two opposing edges to allow mounting of the sample proud of the heater assembly to enable grazing incidence measurements to be made without shadowing from any sample heater components. The dimensions of a typical SXRD sample have been already been given in Figure 4.3 (see Section 4.2.2).
Figure 4.7 Schematic diagram of the experimental arrangement for real time Auger electron spectroscopy (AES).
Figure 4.8 A typical, differentiated measured AES spectrum for Cu(001).
Silicon Substrates

The silicon samples were cut from thick, pre-polished or unpolished wafer at the University of Manchester (Hart). When necessary, samples were polished at the University of Manchester and also at the FOM Institute, Amsterdam (Koper). The Si(001) and Si(111) samples were then degreased and given a wet chemical etch, similar to RCA method (Kern 1984), prior to insertion into the vacuum chamber. The chemical etch removes contaminated Si layers (inherent in wafer production and exposure to air) and replaces the surface with a "clean" oxide layer, to protect the sample during transfer through air, which can be thermally desorbed at UHV. Full details of the chemical etch procedure are given in Appendix A, being a slight modification on that described elsewhere (Finney 1992).

This procedure produces contamination free (within the detection limits of AES), well-ordered Si surfaces with large reconstructed areas. Figure 4.10 shows a 2x1 fractional order peak from the clean Si(001) surface, corresponding to a surface correlation length of 2060 Å (FWHM=0.017°).

Temperature measurement is performed using a calibrated IR pyrometer in conjunction with a neutral density filter. Below 500°C Si is semiconducting and transparent to electromagnetic radiation with a wavelength in the detector waveband and a calibration of the power dissipated by the sample heater vs. the potential drop across the thermocouple is used. This is less accurate than using the pyrometer due to filament movement and differences between individual sample heaters. Above 500°C, the sample temperature is measured using the IR pyrometer.

Copper Substrates

The Cu(001) substrates were spark-cut, to within 0.2° of the (001) crystallographic axis, at the Department of Metallurgy and Materials, University of Birmingham (Sutton) from a copper boule of 99.9999% (6N) purity to the dimensions of Figure 4.3. After ultrasonic cleaning in "Aristar" IPA, each sample was carefully electropolished in a 60:40% orthophosphoric acid:H2O solution to produce a bright "orange peel" finish, followed by rinsing in a (warm) dilute orthophosphoric acid solution, de-ionised water, methanol and then drying. In vacuo, sample preparation consisted of Ar ion sputtering (800 eV) and annealing (700°C) cycles repeated until a sharp (1x1) LEED pattern was observed with no contamination detectable by AES. Full details of the electropolishing method can be found elsewhere (Binns 1981).
4.9 Example of an AST plot for the growth of In on Si(001) at 300 K. The overlayer (In MNN 410 eV) and substrate (Si KLL 92 eV) Auger emission was simultaneously monitored.
Figure 4.10 The (0, 1.5, 0.16) fractional order peak from the clean Si(001)2x1 reconstructed surface. FWHM=0.017° giving a correlation length on the surface of 2060 Å.
Gallium Arsenide Substrates

The GaAs substrates used for the SXRD experiments described in chapter 8 of this thesis were produced from commercially available 0.5 mm thick wafer with a 3000 Å GaAs(001) MBE epilayer and a thin (a few hundred Å) amorphous As (α-As) cap grown on it at the DRA, Malvern (Johnson). The α-As cap protects the GaAs(001) surface during exposure to air. The capped GaAs wafer was cleaved into 8×8 mm² pieces and indium mounted to clean Mo backing plates (of dimensions 8×10×1 mm³) to mimic a standard x-ray sample (see Figure 7.1). The α-As cap was thermally desorbed under UHV conditions by annealing the sample to 450°C to produce a clean, reconstructed GaAs(001)4×1 surface. Full details of the cleaving and mounting procedure can be found in Appendix A.

4.3 Surface X-Ray Diffraction Measurements

4.3.1 Synchrotron Radiation

All the synchrotron radiation measurements described in this thesis were performed at the SRS at Daresbury Laboratory on the wiggler beam line station 9.4, which is designed for surface x-ray diffraction measurements. The SRS operates at an energy of 2.0 GeV. When electrons are accelerated radially in a circular orbit, electromagnetic radiation is emitted. For low energy electrons, the radiated energy distribution is torroidal in shape, but in a synchrotron or storage ring the velocity of the electron’s is very close to that of the speed of light \( (v = c) \) and relativistic effects cause the radiated energy distribution to be concentrated in the direction of the electrons velocity (in the frame of reference of the laboratory). Figure 4.11 illustrates the radiated energy distributions for the two cases. The synchrotron beam is naturally collimated in the vertical direction with a typical spot size ≤ 1 mrad for an energy > 5 keV. In the ideal case, effects due to angular divergence and a finite beam size can be neglected.

The effect is to produce a well collimated, continuous, intense beam of radiation which is almost completely polarised in the orbital plane. The critical (or peak) wavelength of the source, \( \lambda_c \), is defined as (Walker 1986):

\[
\lambda_c = \frac{4\pi\beta}{3\gamma^3}
\]  

(4.1)

where \( \gamma \) is the relativistic factor, and \( \beta \) is the orbit radius.
Figure 4.11 Angular intensity distributions of (a) slow, and (b) relativistic electrons in a circular orbit (Tomboulain and Hartman 1956).
The critical wavelength is defined such that half of the total power emitted has a longer wavelength than $\lambda_c$, and half a shorter wavelength. For the 2 GeV synchrotron radiation source at Daresbury Laboratory $\lambda_c$ is \(\sim 4\) keV (expressed in energy) for a conventional bending magnet ($B \sim 1.2$ Tesla), and $\lambda_c \sim 15$ keV for a wiggler magnet (5 Tesla). The peak intensity occurs at \(\sim 0.7\) $\lambda_c$. Radiation from a bending magnet is linearly polarised when observed in the bending plane (it is elliptical out of plane).

The relativistic factor is given by:

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{E}{m_e c^2} = \frac{eBp}{2m_e e^2}$$  \hspace{1cm} (4.2)

where $E$ is the energy of the orbiting electron, $v$ is the velocity of electron, $c$ is the speed of light, $m_e$ is the rest mass of an electron, $B$ is the magnetic field strength, and $e$ is the charge of an electron.

Synchrotron radiation occurs in a narrow cone of nominal angular width \(\sim \frac{1}{\gamma'}\).

### 4.3.2 X-Ray Beam line Station 9.4

The arrangement of surface x-ray diffraction beam line 9.4 is shown in Figure 4.12 (Norris et al 1992). The multipole wiggler (an insertion device) is placed in a straight section of the storage ring between bending magnets and consists of three liquid helium cooled superconducting magnets. The magnetic field of the wiggler varies sinusoidally (in the horizontal plane) and when electrons pass through the periodic magnetic structure radiation from different parts of the electron trajectory add coherently. The wiggler is better described as a wavelength shifter and its intense magnetic field force the electrons to follow a path whose radius of curvature is smaller than that of the bending magnets, resulting in a radiation spectrum shifted to higher energy, and therefore a shorter critical wavelength than that obtained from the conventional bending magnets. A higher energy in the region of 1 \(\text{Å}\) x-rays is obtained ($\lambda_c \sim 1.3$ \(\text{Å}\)) which is well suited to x-ray structure determination.

Station 9.4 is an end station and utilises the central component of a fan of x-ray radiation produced by the wiggler magnet. In the hard x-ray region, where the
Figure 4.12  Schematic diagram of beam line 9.4 of the SRS at Daresbury Laboratory, UK.
refractive index is close to unity, refracting optics cannot be used and therefore reflecting optics are employed. The central 4 mrad component of the 63 mrad fan is collected by a double focusing torroidal mirror, located 18.2 m from the synchrotron source, inclined at 5.5 mrad to focus the x-rays onto the sample (38 m from the source) (Norris et al 1992). Figure 4.13 shows the profile of the focused wiggler radiation illustrating the typical "bow tie" shape predicted for the mirror from ray tracing analysis.

A water cooled, upwards deflecting, channel-cut Si(111) monochromator (Cernik & Hart 1989), located in the experimental x-ray hutch 36.5 m from the source, is employed to select the wavelength of radiation required. The spectral distribution of the focused beam at the image plane gives $\lambda_\circ \sim 1.3$ Å. Numerous masks and slits along the beam line define the beam and reduce background radiation levels. Typical background levels, with no sample is in the beam, were 0.1 counts s$^{-1}$.

A small air-filled ion chamber positioned after the end of beam (EOB) line slits, and separated from the evacuated monochromator vessel by a small Be window, monitors the (monochromated) incident beam flux. The EOB slits are centre opening and define the footprint of the beam on the sample. After the EOB slits the x-ray beam passes through a $200^\circ \times 30^\circ$, 0.5 mm thick Be window and is incident upon the sample. There is a small air gap between the EOB slits and the Be window to allow movement of the diffractometer without interfering with the beam line. Radiation diffracted from the surface of the sample passes through the same Be window and is collected by a solid state, liquid nitrogen cooled, hyper-pure Ge detector with a maximum count rate of $\sim 5 \times 10^4$ counts s$^{-1}$. Two sets of 4 jaw slits collimate the beam and define the amount of radiation that is detected as well as the resolution in the direction perpendicular to the surface. To reduce air scattering attenuation of the diffracted radiation an evacuated (or He filled) pipe, capped with mylar windows, is placed between the Be window and the Ge detector. The design and performance of the beam line is described elsewhere in detail (Norris 1992).

4.4 Diffractometry

4.4.1 Five-Circle Diffractometer and Sample Alignment

A vertical scattering geometry is employed with the diffractometer to take advantage of the polarisation and better vertical resolution of the synchrotron beam. Figure 4.14 shows a schematic view of the 5-circle diffraction geometry,
Figure 4.13    The focused beam profile obtained with a 100 (horizontal) \( \times \) 50 \( \mu \)m (vertical) slit scanned across the image plane.
Figure 4.14  Schematic diagram of the six circle diffractometer on station 9.4 of the SRS at Daresbury Laboratory, UK.
with the addition of a sixth circle (discussed later), used for SXRD diffraction experiments.

The position of the environmental chamber on the diffractometer precludes the use of a standard chi-circle (χ) and it is replaced by two arcs of limited movement (±20°). A fifth circle (α) allows the grazing angle to be set independently and increases the volume of reciprocal space that can be accessed. In practice, this is restricted by the dimensions of the Be window on the UHV chamber and the position of the beam line. The 6-circle diffractometer described in this section was not used in its out of plane mode since it was not fully operational at the time of the measurements contained in this thesis. The out of plane detector assembly was fitted to the diffractometer, but measurements were performed in the conventional straight-through (γ=0°) mode, being equivalent to the original 5-circle diffractometer geometry.

The volume in reciprocal space that can be accessed under various conditions is shown in Figure 4.15. It corresponds to an x-ray wavelength of 0.8 Å with a beryllium window that subtends an angle of 20° to the sample plane and a maximum movement of the detector arm in the vertical plane of 140° (δ). The detector is in the usual position with its axis perpendicular to the delta axis. For comparison, the accessible volume of reciprocal space for a LEED experiment operating at normal incidence and with electron energy up to 150 eV, is also shown. Thus for the determination of interatomic distances, SXRD gives better inplane accuracy (about ±0.02Å) than out of plane (±0.10Å). The converse is true for LEED.

The accessible region of reciprocal space along the surface normal can be increased by adding a sixth table on the detector arm, with its axis orthogonal to the delta axis. This is, however, expensive and it limits the weight of the detector and introduces some redundancy in the control system since the chi arcs already provide the necessary fine movement. A simple solution to this problem has been provided involving a two-position mounting with γ=0° and γ=15°, where γ is the out of plane angle of the detector, which defines two overlapping regions of accessible reciprocal space. The mounting is sturdy enough to hold a large liquid nitrogen cooled solid state Ge detector. The technical details of the out of plane detector can be found elsewhere (Taylor et al 1994).

A vertical scattering geometry is necessary to accommodate the polarisation of the synchrotron radiation source; for a horizontal scattering geometry the polarisation of the source can lead to near zero polarisation factors for scattering angles near 2θ=90°. Each of the four standard diffractometer circles has a
Accessible region of reciprocal space for Si(111)

Figure 4.15 Diagram of the region of reciprocal space accessible by SXRD and LEED measurements.
resolution of 8,000 steps per degree and the rotary table has a resolution of 10,000 steps per degree, producing precise circle movement and high repeatability. The control of the diffractometer is fully automated with each circle individually controlled by digital electronic computers using feedback circuits to ensure smooth and efficient movement. The x and z directions of the diffractometer are also computer controlled. The diffractometer circles are driven by DC motors with optical encoders to precisely measure the circle positions. The time that the motors are engaged in moving between measured diffraction peaks is significant and the speed of the motor movement has recently been increased to allow more efficient data collection. New zero backlash motors, gearboxes, couplings and amplifiers were installed for the \( \chi, \phi, \alpha \), and \( \delta \) circles and use made of the second encoder on the McLennan 304 intelligent servo controller to aid velocity feedback. A factor of three increase in speed is obtained for these axes, whilst maintaining stability and resolution. The benefit is quicker alignment and movement between peaks in reciprocal space. The time taken for a scan through a single peak is similar, however, the overall time taken to perform a complete rod scan is reduced.

In normal operation the physical surface normal of the sample is coincident with the horizontal axis of the diffractometer so that the Bragg rods are set parallel to the asymmetric resolution function of the detector. The fifth \( \alpha \) circle compensates for the restricted \( \chi \) arc movement necessitated by the presence of the environmental chamber. The accessible region of reciprocal space is a flat disc parallel to the sample surface. The incident and exit angles of the x-ray beam, \( \beta_{\text{in}} \) and \( \beta_{\text{out}} \) respectively, may be independently and exclusively fixed at a constant value or set equal to each other.

A Canberra solid state Ge detector, with a dynamic range of 1 to \( 5 \times 10^4 \) counts s\(^{-1}\), is used for x-ray detection. A hyper-pure Ge crystal, 14 cm in diameter is the detection medium. The Ge crystal is cooled to liquid nitrogen temperature to reduce thermal excitations. An incident x-ray causes excitation of the crystal and a potential applied across the crystal induces multiplication of the charge produced by the incident photon. The signal is amplified and fed into the VME data acquisition system.

### 4.4.2 Crystallographic Sample Alignment.

Initial alignment of the sample (non-crystallographic) is achieved using three circles of the diffractometer. The physical surface normal of the sample is set parallel to the horizontal axis of the diffractometer using a low divergence laser.
Plate 4.3  Photograph showing the out of plane detector assembly.
beam which is reflected off the sample surface. The circles $\phi$ and $\chi$ (see Figure 4.14) are adjusted so that the sample may be rotated through 360°, using the $\omega$ circle, with only minimum movement ($\pm 1$ mm) of the reflected laser spot on a screen positioned 4 m from the sample, approximately normal to the direction of the laser beam.

Crystallographic alignment is achieved by optimising the intensity of particular out-of-plane, bulk $(hkt)$ Bragg reflections. The UB matrix, which interprets between the reciprocal space position and the diffractometer circle positions, can be accurately determined by careful optimisation of two out-of-plane Bragg reflections and refinement made by finding a third reflection. Further angle calculations are made using the UB matrix and $\phi$ and $\chi$ offsets (Vlieg 1987a).

4.5 Data Collection and Reduction

The structure factors used for data analysis are determined from the integrated intensities of measured diffraction peaks. The detector in-plane slits (vertical slits) are wide open to integrate in one direction, with integration in the other direction achieved by rotating the sample about its surface normal (the $\phi$-axis of the diffractometer). This $\phi$-scan moves the diffraction rod through the Ewald sphere (see Section 4.3, Vlieg 1989b). The out-of-plane detector slits (horizontal) determine the length of the rod cutting the Ewald sphere and hence the resolution in perpendicular momentum transfer, $\ell$. The integrated intensity is normalised to the absolute intensity of the incoming x-ray beam as measured by the EOB ion chamber (Section 4.2.2).

The structure factor of measured diffraction peak is calculated after first fitting a Lorentzian curve shape to the peak, in order to determine the peak background, then numerically integrating the area under the peak subtracting the background determined from the Lorentzian fit. The structure factor is calculated from the numerically integrated intensity taking account of correction factors. A rod scan depicts the variation of the structure factor along a direction perpendicular to the sample surface and consists of transverse momentum scans ($\phi$-scans) measured as a function of Miller index $\ell$. Each point on the rod represents a structure factor amplitude obtained from the corrected measured integrated intensity (see Section 4.5.1).
4.5.1 Correction Factors

Geometric correction factors need to be applied to the measured integrated intensities in order to obtain the value of the structure factor.

Area Correction

The area of the sample illuminated by the incident beam and collected by the detector, the *active area*, is defined by the size of the pre-sample (EOB) and detector slits, and the angular position of the detector (diffractometer angle $\delta$). Depending on the width of the beam incident on the sample, defined by the pre-sample horizontal slits, the sample will be *flooded* in the horizontal direction up to a particular angle of incidence, $\beta_{in}$, as illustrated in Figure 4.16. Using focused radiation means that the beam diverges beyond the pre-sample (EOB) slits giving a minimum width of 300 $\mu$m in the direction perpendicular to the sample (the $\ell$ direction). For angles of incidence $\beta_{in} < 4^\circ$, the *footprint* of the incoming beam is larger than the sample in the horizontal direction and consequently the substrate is flooded. Above this angle of incidence the footprint of the beam constantly changes with $\beta_{in}$.

The *active area* is therefore the parallelogram defined by the pre-sample and detector slits. The size of *active area* $A$ is given by:

$$ A = S_1 S_2 \sin \delta $$

where $S_1$ and $S_2$ are the slit settings, and $\delta$ is the angular position of the detector (we may approximate $\delta \approx 2\theta$).

The diagonal length, $d$, of the parallelogram is given by:

$$ d = \frac{S_1^2 + S_2^2 + 2S_1 S_2 \sin \delta}{2 \sin \delta} $$

$S_1$ and $S_2$ are kept fixed during experimental measurements and so the correction factor applied to the measured integrated intensity is $\frac{1}{\sin \delta}$.

The correction is valid provided that $d$, the diagonal length, does not exceed the borders of the sample. For such situations additional corrections have to be made to account for the beam *falling off* the sample. This is important for small scattering angles ($2\theta$) and larger errors are associated with the structure factor values for these diffraction peaks near the reciprocal space origin. This is partly
Figure 4.16  Collimating slit arrangement for SXRD measurements. The shaded parallelogram is the active area in the experiment.
overcome by increasing the wavelength of the incident radiation and measurements at small scattering angles are made at 1.38 Å, which also has the added benefit of increased flux.

**Inverse Lorentz Factor**

It can be shown (Marra 1979, Sinha 1988) that the total intensity measured in a φ-scan is essentially an integration over an area element of the diffraction rod, which varies as a function of δ and β (28). The inverse Lorentz factor corrects for the dependence of the measured intensity on the position at which the Ewald sphere cuts the diffraction rod. The inverse Lorentz correction factor is given by (Hahn 1983):

\[ L = \sin 2\theta \cos \beta \]  

(4.5).

**Polarisation Factor**

The linear polarisation of the synchrotron beam in the horizontal plane means that a correction must be applied to the integrated intensities when measurements are performed away from the vertical scattering plane. The polarisation factor depends on the polarisation of the incoming beam and the direction of observation relative to the beam and is defined as:

\[ P = \frac{1}{(\sin^2 \delta + \cos^2 \delta \cos^2 \alpha)^{\frac{1}{2}}} \]  

(4.6)

It is dependent on angles α and δ, and not the sample position. A derivation of the polarisation factor can be found elsewhere (Warren 1969).

**The Structure Factor**

The structure factor amplitude for a given (hkl) reflection, \(|F_{\text{hkl}}|\), can be therefore calculated by taking the square root of the integrated intensity after applying the above correction factors, as shown below:

\[ |F_{\text{hkl}}| = \sqrt{\frac{\sin^2 \delta \cos \beta}{\sin^2 \delta + \cos^2 \delta \cos^2 \alpha}} \frac{1}{I_{\text{hkl}}} \]  

(4.7)

where \(I_{\text{hkl}}\) is the measured integrated intensity (The approximation \(2\theta = \delta\) is applied again).
4.5.2 Agreement Criteria

Reduced $\chi^2$ test

A reliable test of the ability of a model to reproduce the experimentally observed data is the reduced $\chi^2$ test,

$$\chi^2 = \frac{1}{N - p} \sum_{\text{all}} \left( \frac{|F_{\text{calc}}| - |F_{\text{meas}}|}{\sigma_{\text{tot}}^2} \right)^2$$

(4.9)

where $N$ is the number of structure factors,

$p$ is the number of free parameters (including the scale factor), and

$\sigma_{\text{tot}}^2$ is the uncertainty on $|F_{\text{meas}}|$ (Sinha 1988, Robinson 1991).

The reduced $\chi^2$ test is an extension of the least squares fitting procedure giving the quality of the proposed fit. A full justification can be found in Bevington (1969).

4.6 Analysis Procedure

The structure factor amplitudes for a limited region of reciprocal space are obtained from the experimentally measured integrated intensities and are related to the unit cell structure by the Fourier transform of the electron density, and it is therefore not possible to directly invert the data to yield the structure. A unique solution needs to be found and not a local minimum which may be reached by testing trial structures. Calculation of the Patterson function (Section 3.2.5) from the experimental data yields useful information about the real space structure, obtained from the interatomic vectors within the Patterson function. From this, a trial model for the structure can be proposed and then refined. The model obtained from the Patterson function can be surprisingly close to the actual structure given the limited data set and the effects of intrinsic peak broadness. Refinement of the atomic positions is performed using a computer program to minimise the least squares residuals on the $\chi^2$, with a satisfactory model obtained with a $\chi^2$ of close to unity, i.e. the measured and calculated structure factors agree within experimental error.

The model is optimised by fitting the experimental structure factors to the theoretical structure factors, calculated from the initial model, by:
\[ F_{hkl} = \sum_j f_j \exp \left[ -\frac{B_j q^2}{16\pi^2} \right] \exp \left[ -2\pi i (hx_j + ky_j + lz_j) \right] \]  \hspace{1cm} (4.10)

where \( B_j \) is the isotropic factor,
\( q \) is the momentum transfer associated with the point in reciprocal space, and
\( f_j \) is the atomic form factor of the \( j \)th atom.

The inclusion of in-plane integer order structure factor amplitudes allows the registry of the surface unit cell with respect to the substrate lattice to be determined. The atomic displacements perpendicular to the surface can be determined from out-of-plane intensity measurements, known as rod scans, with the structure fixed at the lateral geometry found from the in-plane data. Finally, the in-plane and out-of-plane data are fitted simultaneously to fully determine the overlayer structure.

### 4.6.1 Symmetry and Averaging

For an accurate structure determination it is advisable to measure integrated intensities from several symmetry equivalent reflections. The agreement between equivalent reflections is used to obtain the systematic error that arises from unavoidable misalignment errors. The total uncertainty on a particular intensity, \( I_{hkl} \), is approximated by:

\[ \sigma_{\text{total}}^2 = \left( \sigma_{\text{stat}}^2 \right)^2 + \left( \sigma_{\text{sys}}^2 \right)^2 \]  \hspace{1cm} (4.11)

where \( \varepsilon \) is the systematic error and
\( \sigma_{\text{stat}} \) is the statistical error obtained from curve fitting (Section 4.5.1).

### 4.6.2 Structural Study of a Reconstructed Surface

One needs to measure the integrated intensities of the fractional order reflections in the plane of the surface, i.e. at \( \ell=0 \) (Feidenhans'l 1989). It is, of course, not possible to measure at \( \ell=0 \), due to x-ray absorption. Instead, one measures at a small \( \ell \) value, for example, \( \ell=0.1 \), i.e. above the critical angle yet still small enough to be surface sensitive.
From Friedel's law:

\[ |F_{\bar{m}l}| = |F_{m\bar{l}}| \quad (4.12) \]

Thus, by averaging the integrated intensity values at \( l = \pm 0.1 \) we obtain the structure factor at \( l = 0 \) to a first approximation.
Chapter 5
The Pseudomorphic Growth of Fe on Cu(001)

5.1 Summary

This chapter discusses the MBE growth of Fe on Cu(001) studied as a function of Fe coverage and substrate temperature between 85 and 473 K. Fe on Cu(001) is a model heteroepitaxial metal-metal system and is perhaps the most studied, with many conflicting results published. An extensive review of the literature is first given followed by the results obtained by surface x-ray diffraction. Fe growth at 85 K was diffusion limited. The 300 K data are shown to be consistent with kinematical theory and establish that Fe grows on Cu(001) in a layer-by-layer mode forming a tetragonally distorted fcc overlayer with limited Fe-Cu intermixing in the interfacial region. Fitting the specular rod data gave an estimate of the degree of intermixing and the interlayer spacing of the film. Growth at elevated temperatures was disordered due to severe intermixing. The last section deals with the effect of adsorbed gases at the surface on the growth of the Fe overlayers. In the next chapter more detailed measurements at specific Fe coverages are presented enabling the perpendicular film structure to be determined.

5.2 Background

Iron can exist in several allotropes (see Chapter 2, Figure 2.1). At ambient pressures and from low temperatures up to 910°C the stable phase is a bcc structure which is ferromagnetic. The lattice constant, \( a_0 \), is 2.867 Å with a near neighbour distance \( (a_{\text{nn}}) \) of 2.482 Å (Wyckoff 1971). Between 910°C and 1390°C iron crystallises in an antiferromagnetic fcc (\( \gamma \)-Fe) phase with a lattice constant of 3.647 Å (Pearson 1958). From 1390°C to the melting point of 1534°C Fe exists in a non-magnetic bcc phase (\( \delta \)-Fe). Extrapolation to 20°C using the thermal expansion coefficient of the \( \gamma \)-Fe phase gives a value of \( a_0=3.59 \) Å \( (a_{\text{nn}}=2.54 \) Å) for iron in an fcc arrangement (Glatzel et al. 1991). This is only 0.7% smaller than the lattice constant of fcc copper \( (a_0=3.615 \) Å, \( a_{\text{nn}}=2.556 \) Å). Since iron and copper are mutually immiscible in the bulk (Hansen 1958) it should be possible to form the fcc phase of Fe by epitaxial growth on a copper substrate, as shown in Figure 5.1(a). Against this, the large difference in surface free energies of iron (2150 mJ/m²) and copper (1850 mJ/m²) (Miedema 1978, 1980a, b) would suggest that a monolayer of iron on copper is not energetically stable. For successful layer-by-layer growth the sum of the adsorbate surface-free energy and the interfacial free energy must be less than the surface free energy of the
substrate. Bauer (1958) predicted the formation of Fe islands on the Cu(001) surface. Epitaxial growth, however, is a dynamic process far from equilibrium and microscopic mechanisms can strongly influence the growth. γ-Fe may also be stabilised in a Cu or CuAl matrix as small particles (Ezawa 1989, Newkirk 1957).

This prototypical system was thought to be ideal for studying the simple overlayer formation of two closely lattice matched metals, but has proven to be far more complicated than originally suspected, yielding many controversial and contradictory experimental and theoretical results.

Although it is generally accepted that iron grows on the (001) face in a strained fcc phase (see Figure 5.1(a)), the details of the growth, especially in the low coverage regime up to 5 monolayers (ML), and the eventual relaxation to the bulk bcc Fe (α-Fe) phase at higher coverage (Figure 5.1(b)), remain a matter of much controversy.

Experimental studies of Fe on Cu(001) date back to 1956 (Haase), however, the first reliable UHV results for the stabilisation of the fcc Fe phase by epitaxial growth on Cu(001) were by Jesser and Matthews (1967, 1968) using electron microscopy, who found that Fe deposits on Cu(001) were fcc and strained to exactly match the copper substrate. Chambers et al (1987) prepared good quality films of Fe on Cu(001) at room temperature up to a coverage of 5 monolayers (ML), determined by Auger electron diffraction (AED) and low energy electron diffraction intensity analysis (LEED I/V). At low coverage, growth proceeded through the formation of two-layer deep clusters which formed well-ordered, flat layers by a coverage of 3 ML. Deposition at elevated substrate temperatures (398 K) promoted interdiffusion of Fe adatoms and the substrate displacing Cu atoms at lattice sites.

Newstead (1987) showed the growth of Fe on Cu(001) to develop in a layer-by-layer mode at 300 K up to a coverage of 4 ML. This was confirmed by Germar et al (1988) who observed a layer-by-layer growth mode at 300 K by recording the Auger amplitude as a function of deposition time. A detailed AES study (Glatzel et al 1991), however, suggested a bilayer growth mode for the first two bilayers, with the Auger breakpoints corresponding to bilayer completion, confirmed by Rutherford back scattering (RBS) analysis. LEED showed the Fe overlayer to have a (1×1) pattern indistinguishable from the clean Cu substrate pattern.
Figure 5.1 Schematic diagram of the lattice matching of (a) fcc Fe(001) on Cu(001), and (b) bcc Fe(001) on Cu(001). The case of perfect epitaxy is illustrated, which implies that the atomic spacing in the overlayer is smaller in (b) than in (a). In reality the fcc lattice experiences an inplane expansion on the Cu(001) surface, and bcc Fe will not grow with perfect epitaxy directly on the bulk Cu surface because the strain is too great. $a_1$, $a_2$, and $a_3$ illustrate the surface vectors used (defined in Section 5.3). .../continued
(c) fcc Fe(001)/fcc Cu(001)
perfect matching, i.e. \(a_o(Cu) = a_o(Fe) = 3.615 \text{ Å}\)

**Out of plane reciprocal space:**

**In plane reciprocal space (\(\ell = 0\)):**

\[ h = k \]

* lattice positions quoted in surface notation (Section 5.3)

**bcc Fe(001)/fcc Cu(001)**
Fe relaxed and rotated 45° with respect to Cu(001)
\(a_o(Cu) = 3.615 \text{ Å} \) and \(a_o(Fe) = 2.8665 \text{ Å}\)

*Figure 5.1* (c) diagram of reciprocal space for fcc Fe(001) and bcc Fe(001) grown on fcc Cu(001).
A reflection high energy electron diffraction (RHEED) and x-ray photoemission spectroscopy (XPS) forward scattering study (Steigerwald et al. 1987, 1988) suggested Fe agglomeration with double-layer height islands for the first monolayer, followed by a gradual burying of the substrate complete at a coverage of 5 ML. Significant Cu surface segregation onto Fe was reported at room temperature producing an intermixed film. Intermixing became severe at a substrate temperature of 673 K, whereas growth at low temperature (165 K) suppressed the initial Fe agglomeration. Above 5 ML layer-by-layer growth occurred and was comparable to the homoepitaxial growth of fcc Fe on the fcc Fe(001) overlayer. 3 ML thick films were concluded to be the thinnest films that could be prepared with structural integrity.

LEED I-V, medium energy electron diffraction (MEED), and AES results by Thomassen et al. (1992) also supported agglomeration of Fe below a coverage of 5 ML, followed by layer-by-layer growth.

Helium atom scattering (HAS) experiments at room temperature (Arnott et al. 1992, Dastoor et al. 1992) indicated that growth was initially disordered, with a high defect density at 1 ML coverage, following which a simultaneous multilayer mode predominated with the formation of three-dimensional islands. The deposited Fe initially had a reluctance to wet the Cu surface. There was a tendency towards a Frank van der Merwe growth (layer-by-layer) mode from about 2 to 7 ML, above which coverage misfit dislocations caused a deterioration of the film quality. Growth at 420 K showed intermixing in the early stages, determined by AES, whereas growth on a substrate at low temperature (220 K) was diffusion limited.

RHEED measurements by Wuttig et al. (1993) showed irregular intensity oscillations up to a 5 ML coverage, supporting Fe agglomeration, followed by regular oscillations of a monolayer period gradually decaying as epitaxial growth broke down. The Fe film was a distorted fcc structure and varied LEED reconstructions were observed with coverage. Considerable inter-diffusion of Fe and Cu was reported for films deposited at 370 K. STM measurements by Johnson et al. (1993) showed significant intermixing of Fe and Cu in the early stages of growth with the formation of Fe inclusions in the top substrate layer. At a coverage of 2.8 ML a layer-by-layer growth mode was established. A low energy ion scattering (LEIS) study (Detzel et al. 1993) reported distorted bilayer growth up to a 2 ML coverage, with 50 % inclusion of Fe in the top substrate layer, in contradiction to Johnson et al. (1993). A more recent STM study (Giergiel 1994) indicated there to be no intermixing in the initial stages of growth, but did agree that a layer-by-layer growth mode was eventually achieved, but at a coverage of 4 ML.

More recently, RHEED experiments (Schatz et al. 1994) concluded that the room temperature growth of Fe on Cu(001) was in a layer-by-layer-like growth mode, with
bilayer formation in the first two monolayers. For a temperature range of 333-370 K strong, regular RHEED intensity oscillations were observed indicating good layer-by-layer growth over the whole coverage regime. Further STM work by Johnson et al (1994) confirmed the earlier suggestion of incorporation of Fe into the substrate at low coverage (θ<0.2 ML), which was followed by simultaneous layer growth up to a coverage of 2 ML. Chambliss et al (1994) compared MEED diffraction intensity oscillations (after Thomassen et al 1992) with STM topography measurements, applying kinematical formulae, concluding that poor layer-by-layer growth initially occurred, but improved as the coverage increased and was eventually disrupted by formation of the bcc Fe phase.

Relaxation to the bcc Fe phase was reported to occur at a coverage of about 14 ML, from LEED I-V, MEED, and AES measurements (Thomassen et al 1992, Wuttig et al 1993). An STM study by Giergiel et al (1994) showed that fcc Fe films exhibited structural instability at a coverage as low as 4.6 ML, attributed to the formation of a dislocation network, being a precursor to bcc Fe formation.

In a LEED I/V investigation of the structure of Fe films on Cu(001) at 300 K, up to an Fe coverage of 7 ML, Clarke et al (1987) correlated changes in the film structure as a function of coverage with magnetic behaviour suggesting that expansion of the film interlayer spacing could be responsible for the observed ferromagnetism (Pescia et al 1987). An extended x-ray absorption fine structure (EXAFS) study (Magnan et al 1991a, b) confirmed that the overlayer structure was coverage dependent displaying structural re-ordering with film thickness. Anti-ferromagnetism was associated with an fcc Fe structure, whilst ferromagnetic films had a distorted fcc structure.

For the epitaxial growth of Fe on Cu(001) contradictory magnetic behaviour has been reported which finds Fe to be anti-ferromagnetic (Macedo and Keune 1991), non-magnetic (Bader and Moog 1987), ferromagnetic (Allenspach and Bischof 1992, Liu et al 1988), and possessing surface ferromagnetism (Thomassen et al 1992). Perpendicular surface anisotropy was observed in ferromagnetic films (Liu et al 1988). The magnetic phase diagram for the Fe/Cu(001) system has been determined by Donqui et al (1994) who identified three magnetic regions as a function of Fe coverage and growth temperature (see Chapter 6, Figure 6.1), and concluded that the metastable fcc Fe phase is subject to strain and lattice distortion producing diverse magnetic states.

It is obvious that there is significant disagreement over the initial overlayer growth, even for studies using the same technique. Three distinct growth regions, however, have been identified and there is general agreement that layer-by-layer growth occurs over a 5 to 10 ML coverage range, followed by a phase transition to bcc Fe
phase at a critical coverage determined by the growth conditions. The growth of Fe on Cu(001) is unusually dependent on the growth conditions and disagreement between different groups may be due to different sample preparation and MBE conditions.

Surface x-ray diffraction (SXRD) is well established as a powerful probe of surface crystallography. The weak scattering of x-rays allows a simple interpretation of measured intensities through the kinematic approximation, thus giving a direct and immediate insight into the atomic geometry. The technique has recently been extended to provide real time monitoring of surfaces during epitaxial growth (Finney et al 1992). This thesis reports the first SXRD study of the structure and morphology of epitaxial Fe films grown on Cu(001) up to a coverage of 38 ML for a substrate temperature range from 85 K to 473 K.

5.3 Experimental Details

The copper single crystal substrates were spark-planed to within 0.2° of the (001) crystallographic axis and electropolished to produce a bright ‘orange peel’ finish. Successive cycles of Ar ion bombardment and annealing at 600°C were made in vacuo until contamination levels were below that detectable by AES. LEED studies of samples that had been polished by mechanical methods indicated surfaces of inferior quality to those prepared by the above method. Fe, of purity 99.998%, was deposited from a water-cooled Knudsen cell at deposition rates between 2 and 16 minutes per monolayer, confirmed by Rutherford back scattering (RBS) analysis. During deposition the base pressure increased from 1x10^-10 to 5x10^-10 mbar.

We define one monolayer as the density of a single (001) layer of bulk Cu, i.e. 1.53x10^15 atoms cm^-2. The momentum transfer is expressed by Miller indices h, k, and ℓ, referred to the Cu fcc unit cell with dimensions of a_b is 3.615 Å. For Cu(001) the surface unit mesh is defined with respect to the bulk unit cell by two orthogonal vectors a_1 and a_2 given by 1/2[110]_bulk and 3/2[110]_bulk respectively (see Figure 5.1).

5.4 The Growth of Fe on Cu(001)

5.4.1 Specular Reflectivity Monitored During Growth

The specular reflectivity, which is measured from grazing incidence out through Bragg reflections, is independent of in-plane structure since the component of
momentum transfer parallel to the surface is zero. Specular reflectivity provides a simple but effective way to obtain information such as layer thickness, thickness fluctuations, degree of strain, crystallinity and defect density, allowing determination of the growth morphology on an atomic scale. Increasing surface roughness manifests itself as a gradual damping of the measured intensity. Useful information may be derived from the interference effects that occur around Bragg peaks, where interference fringes arising from \(N\) atomic layers with spacing \(d\) (in a semi-infinite crystal) induce an oscillatory factor due to the interference from the two interfaces, essentially acting as a free standing crystal.

Growth mode determination begins by monitoring the variation in specular intensity as a function of deposition time at a fixed point along the specular rod. A first estimate of the interlayer spacing of the Fe overlayer can be derived from analysis of the specular growth curve measured in such a way (Finney et al 1992), however, the accuracy of the layer spacings obtained is limited since only a single point in reciprocal space is sampled. Also, epitaxial growth is a dynamic process far from equilibrium and the overlayer structure may rearrange after deposition. A further consideration which may affect the as-deposited overlayer is the change in structure as a function of film thickness. The detailed perpendicular morphology at the surface is more accurately determined from analysis of diffracted intensity measured as a function of perpendicular momentum transfer, \(\ell\). This is addressed in more detail in the next chapter.

5.4.2 Growth as a Function of Temperature

Figure 5.2 summarises the variation in specular intensity with Fe deposition time at different substrate temperatures (the Fe shutter was opened at time \(t=0\) minutes). The data were recorded at the anti-Bragg position on the specular rod, i.e. \((h=0, k=0, \ell=1)\). It is midway between the origin and the first Bragg point and the reflected waves from adjacent layers are out of phase at this position.

At 85K there is a rapid drop in intensity after opening the Fe shutter showing that the growth was diffusion limited and poorly ordered, i.e. the surface mobility of the adsorbate atoms was reduced at low temperature. The effect of the low temperature surface was to suppress thermally activated diffusion. At 300 K well-defined, regularly spaced intensity oscillations, indicative of layer-by-layer growth, are observed. Each peak is attributed to the completion of successive monolayers. The coverage at the peak maximum was independently confirmed to be 1 (±0.2) ML by RBS analysis (a large error is associated with this value since the RBS calibration was
Figure 5.2 Growth of Fe on Cu(001) monitored at the anti-Bragg position of the specular rod at the substrate temperatures indicated. Fe evaporation was started at t=0 minutes.
Figure 5.3  The growth of Fe on Cu(001) at a substrate temperature of 373 K whilst simultaneously monitoring (a) the AST (Cu 60 eV emission line) signal and (b) the x-ray specular reflectivity at (0, 0, 1) as a function of Fe deposition time.
performed on a thin film of Fe). The progressive damping of the oscillations was due to increasing surface roughness. The measured x-ray data are consistent with Auger signal versus time (AST) plots of Newstead (1987) which showed a series of linear breaks immediately after opening the shutter. At 373K, the oscillations are weaker and the period of the first oscillation is almost double that of the subsequent oscillations, suggesting the formation of an initial bilayer. At 473K no oscillations are observed due to significant Fe-Cu intermixing at this temperature resulting in poor overlayer growth (Arnott 1992).

Simultaneous measurements of the x-ray intensity and AST signal can be made during Fe deposition. Figure 5.3 illustrates the results obtained for the growth of Fe on Cu(001) at 373 K. The AST plot shows no breaks and the x-ray signal (reproduced from Figure 5.2) is irregular in period and heavily damped showing poor layer growth. For Fe growth at 300 K the AST signal, previously measured by Newstead (1987), has regular breaks indicating a layer-by-layer growth mode.

From a visual inspection of the real time x-ray intensity oscillations we can derive qualitative information about overlayer island formation. Essentially, a rapid fall to low intensity indicates effective coverage of the substrate by overlayer atoms, however, information of a more qualitative nature can be gained by kinematical analysis of the measured curves, as described in the next section.

Quantitative Analysis of Growth at 300 K

The oscillatory behaviour of the x-ray signal at 300K can be quantitatively understood using kinematical scattering theory. This has been used to describe x-ray scattering from roughened surfaces and extended to heteroepitaxial growth by Finney et al (1992). The structural model used in the analysis is shown in Figure 5.4. For a bulk terminated Cu(001) surface, in which layers repeat with a period $a_o/2$, the amplitude of the specular beam is given by:

$$ F_{\text{bulk}} = \frac{f_{\text{Cu}}}{1 - \exp \left[ -\pi \ell \mu \left( \frac{a_o}{2\mu} \right) \right]} $$

(5.1)

Here $f_{\text{Cu}}$ is the atomic scattering factor for copper and $\mu (>> a_o)$ is the penetration depth. If Fe is grown on the surface in successive layers, the total scattering amplitude can be written as the sum of the contributions of the bulk and the individual Fe layers as:
Figure 5.4  Model used in fitting the specular intensity measured as a function of deposition time for the growth of 2 ML of Fe on Cu(001) at 300 K. From a kinematical analysis of the intensity the interlayer spacings of the Fe layers can be determined.
Figure 5.5  Fit to initial growth of Fe on Cu(001) using the two layer model described in the text.
where \( z_n \) is the separation of the \( n \)th layer from the copper surface.

This model was fitted to the measured variation of the x-ray intensity with parameters such as deposition rate \( R \) and the vertical displacement of the two Fe layers, \( z_1 \) and \( z_2 \), treated as free parameters (see Figure 5.4). A scale factor, to account for the experimental geometry, was determined from the clean Cu(001) surface signal, which was considered to be an ideal termination of the bulk. The background level was obtained from a transverse scan at the deposition position before deposition was started. The solid line in Figure 5.5 shows the best fit to the first two oscillations of the measured intensity curve. It corresponds to a reduced \( \chi^2 \) of 1.24 and was obtained with \( R \) equal to 0.077 ML min\(^{-1}\) and \( z_1 \) and \( z_2 \) equal to 1.71\( \pm \)0.1 Å and 3.54\( \pm \)0.1 Å, respectively. The heights of the Fe layers are consistent with the epitaxial growth of an unrelaxed, tetragonally distorted fcc structure. If we assume Cu and Fe atoms at the surface retain the metallic radii of the bulk equilibrium phases, then the Fe structure is expanded in plane by 0.7\% relative to that expected for a close packed fcc Fe structure, the height of the first layer is 1.76 Å and that of the second layer is 3.46 Å. Allowing for the error, the heights are the same as the values deduced from the experiment. A more accurate analysis of the out of plane structure is based on intensity measurements as a function of perpendicular momentum transfer, which contain far more information since a much larger proportion of reciprocal space is sampled (see Chapter 6).

### 5.4.3 Fe-Cu Intermixing at the Substrate-Overlayer Interface at 300 K

Closer inspection of the growth curve measured at 300 K reveals two effects, (i) an oscillatory behaviour observed in consecutive peak heights between 3 and 12 ML, and (ii) the collapse in intensity at \( \sim 12 \) ML coverage. This former result is expected in heteroepitaxial growth but appears out of phase in this instance and is discussed below. The latter effect is due to collapse of the metastable fcc Fe phase to bcc (bulk) Fe structure and is discussed later in section 5.4.6.

The difference in atomic scattering factor between Fe (atomic number 26) and Cu (atomic number 29), albeit small, is evident as a change in intensity at completion of successive monolayers during epitaxial growth, as theoretically illustrated in Figure 5.6(b) for the case of ideal layer-by-layer growth. On completion of the first Fe monolayer the specular intensity has fallen to about 65\% of the starting value due to destructive interference between Fe and Cu atoms. In the case of homoepitaxial growth the intensity regains the initial value at all points corresponding to...
Figure 5.6  Experimentally measured growth curve for the growth of Fe on Cu(001) at 300 K, (b) theoretical growth curve for single layer-by-layer growth of Fe on Cu(001), and (c) theoretical growth curve for single layer-by-layer growth of Fe on Cu(001) including atomic intermixing at the Fe-Cu interface, with 50% incorporation of Fe into the substrate.
Figure 5.7  Analysis of the specular growth curve for deposition of Fe on Cu(001) at 300 K (shown in Figure 5.2). The figure shows the difference in successive peak heights (background subtracted) with Fe coverage (dashed line) and (b) the extremely regular period of the growth oscillations, least squares fitted with a straight (solid) line, giving an $r$ factor of 1.0.
monolayer completion. After deposition of 2 ML of Fe the specular intensity reaches the initial value since the scattering from the two (ideal) Fe layers is out of phase and cancels (as the x-ray beam penetrates the adlayer attenuation will occur but this has not been included here since we merely intend to illustrate the effect of the difference in scattering factor between Cu and Fe). The pattern repeats itself as a function of Fe coverage.

STM studies by Detzel et al (1993) and Chambliss et al (1994) suggested that growth of Fe on Cu(001) at 300 K begins by incorporation of Fe atoms into the Cu substrate forming discrete inclusions and displacing Cu atoms into the growing Fe overlayer. The Cu atoms form small monolayer islands and Iron atoms subsequently decorate the island edges. The result is a heterogeneous first subsurface layer and first Fe monolayer in which Fe is found in equal amounts (Detzel, 1993). The lattice sites are randomly occupied by Fe and Cu atoms. Other studies have confirmed this behaviour (Steigerwald et al 1987, Chambers et al 1987, Johnson et al 1993, 1994)

Comparison of the ideal layer-by-layer growth pattern expected for Fe on Cu(001) with the experimentally measured behaviour at 300 K (Figure 5.6(a), reproduced from Fig. 5.2 for convenience) shows a discrepancy of 1 ML. The measured data displays the above effect from 3 to 12 ML but there is a phase shift of 1 ML between the predicted and measured curves. The effect can be accounted for if intermixing of Fe and Cu is included at the overlayer-substrate interface introducing a one monolayer shift to theoretical curve, as shown in Figure 5.6(c). Fe was included in equal proportions in the topmost substrate layer and first Fe layer. After completion of the first monolayer the scattering from the two intermixed layers cancels and subsequent growth takes the form of that originally calculated curve (Figure 5.6(a)). The effect becomes more pronounced when the measured data are background subtracted, as shown in Figure 5.7(a). Also illustrated is the period of the intensity oscillations with Fe coverage illustrating the remarkable regularity of the layer formation up to a coverage 14 ML (Figure 5.7(b)). A least squares fit to the data is shown (goodness of fit, r=1.0). The period was 15.83±0.5 minutes ML⁻¹.

The Fe-Cu atomic intermixing at the substrate-overlayer interface (Figure 5.8) modifies the total scattered amplitude. The effect of the intermixing on the scattering amplitude can be described in a simple manner if we assume the following approximation. We consider the extreme case in which the Fe layers grow with the same interlayer separation as the copper substrate and describe the scattering at the anti-Bragg position where $l=1$. The total scattering amplitude, $A_{\text{total}}(x)$, is then given by:

$$A_{\text{total}}(x)$$
Here $x$ is the fraction of Fe incorporated into the substrate, $\theta$ is the coverage of Fe, and $f^{Cu}$ and $f^{Fe}$ are the scattering factors for Cu and Fe respectively.

This simple model describes the observed results. If there is no intermixing, i.e. $x=0$, then Eq. (5.3) reduces to $-1/2f^{Cu} + f^{Fe}$ (for the case of $\theta=1$, i.e. 1 ML of Fe deposited) as expected for the simple case of heteroepitaxial layer-by-layer growth. If $x$ equals 0.25, i.e. 25% of the top substrate layer is replaced by Fe atoms and the Fe adlayer consists of 25% Cu and 75% Fe. The total amplitude becomes $1/2f^{Fe}$, which is independent of $f^{Cu}$ and, curiously, the growth behaviour resembles the homoepitaxial growth of Fe.

For the case of $x=0.5$, i.e. Fe is found in equal amounts in the substrate and overlayer (the situation determined experimentally), then the total scattering amplitude is $1/2f^{Cu}$, i.e. equivalent to Cu homoepitaxial growth. For $x$ equals 0.75 an equivalent result is obtained as in the case where $x$ was 0.25, although the intensity at 1 ML is larger, and Eq. (5.3) reduces to $f^{Cu} - 1/2f^{Fe}$, where the $f^{Cu}$ has no effect, resulting in scattering dominated by Fe.

Finally, if the scattering factors $f^{Cu}$ and $f^{Fe}$ are equal (i.e. $f^{Fe}=f^{Cu}$), then the total scattering amplitude $1/2f^{Cu}$ is independent of $x$, which is equivalent to the situation of homoepitaxial growth of Cu on Cu(001).

We can estimate the amount of intermixing at the substrate-overlayer interface for the film deposited 300 K from the experimentally measured growth curve. Many factors play a role in epitaxial growth which are not accounted for in the above model and we therefore expect to gain only an estimate of the extent of intermixing. The experimentally measured intensity is attenuated by a time dependent exponential function, the physical origin of which lies in imperfect layer growth, where the nth layer begins to grow before the (n-1)th layer is complete, giving a gradual decrease in the measured intensity. This is most prominent at the early
Figure 5.8  Schematic diagram of the intermixing model used in the analysis of the specular growth curve at 300 K, where x is the fraction of intermixing (0<x<1), and θ is the total Fe coverage. The Fe and Cu content in the topmost substrate layer is given by Fe_{sub}=(1-x)θ and Cu_{sub}=xθ respectively, and in the first monolayer by Fe_{ML}=xθ and Cu_{ML}=(1-xθ) respectively.
stages of growth and, in consequence, the intensity arising from the formation of the first few oscillations is heavily modified by the damping envelope. A better estimate of the degree of intermixing may be obtained from the intensity variation in consecutive peaks later in deposition (3 to 12 ML coverage), where the damping effects are less dramatic. From such an analysis we obtain a crude estimate for the extent of Fe intermixing of around 35%. This will be shown to be inaccurate by later analysis (see chapter 6) and also disagrees with the value generally reported in the literature. A value of 50% (x=0.5) was therefore taken for the extent of intermixing.

5.4.4 Growth of Fe on Cu(001) Monitored as a function of Perpendicular Momentum Transfer

Glatzel et al (1991) proposed a bilayer growth mode for Fe on Cu(001) at room temperature from AES measurements. Schatz et al (1994) also reported a bilayer mode up to 2 ML. To gain a complete insight into the growth mode of epitaxial systems it is necessary to monitor the epitaxy in-situ at different positions in reciprocal space. The vertical growth morphology is most conveniently determined by recording the intensity variation at different values of perpendicular momentum transfer (ε-value) during deposition.

The growth of Fe on Cu(001) at 300 K was measured at ε=0.5, ε=0.75, and ε=1.0 rlu on the specular rod, i.e. (h=0, k=0, ε). (0, 0, 1) corresponds to the anti-Bragg position where maximum sensitivity to monolayer height island formation is achieved. All other positions are less sensitive to monolayer growth, ultimately being swamped by bulk scattering from a Bragg peak, but nevertheless provides important information about the growth mode. Figure 5.9 shows the experimental results at the above conditions. Each curve was normalised to the initial clean substrate intensity and each deposition was carried out at the same deposition rate, as set by the temperature of the Knudsen source (±2 %).

Deposition of Fe at the (0, 0, 1) position, illustrated in Figure 5.9(b), shows well-defined, regular intensity oscillations with a period of 1 ML. The intensity variation due to the differential scattering of Fe and Cu combined with interfacial intermixing is established by a coverage of 4 ML. Monitoring the overlayer growth at (0, 0, 0.75) shows slightly weaker oscillations but with period of 1 ML in agreement with the calculated curve (Figure 5.10(b)). The results recorded for Fe deposition monitored at (0, 0, 0.5) display an oscillatory nature, although poorly defined, with an irregular period. Figure 5.11 shows the results expected if bilayer growth occurs. It is apparent that this is not the situation in the experimentally measured data.
Figure 5.9  
Growth of Fe on Cu(001) at 300 K monitored at different perpendicular momentum transfer values of (a) \( t=1.0 \), (b) \( t=0.75 \), (c) \( t=0.5 \) rlu on the specular rod.
Figure 5.10  Theoretical models for the growth of Fe on Cu(001) at $\ell=1.0, 0.75, 0.5$ rlu on the specular rod for (a) ideal single layer-by-layer growth, and (b) ideal single layer-by-layer growth including 50% Fe-Cu intermixing at the overlayer-substrate interface.
Figure 5.11 Theoretical models for the growth of Fe on Cu(001) at $t=1.0, 0.75, 0.5$ rlu on the specular rod for (a) ideal bilayer growth, and (b) ideal bilayer growth including 50% Fe-Cu intermixing at the overlayer-substrate interface.
Combined with RBS analysis, which confirmed the coverage at the first peak to be one monolayer, a bilayer mode can clearly be out-ruled. Therefore, the measurements as a function of perpendicular momentum transfer support a layer-by-layer growth mode at 300 K. Intermixing at the substrate-overlayer interface was confirmed.

5.4.5 The Effect of Deposition Rate on Growth of Fe on Cu(001)

The effect of deposition rate on the growth of Fe on Cu(001) has been investigated by measurements at the anti-Bragg position of the specular rod. Figure 5.12 shows the growth of Fe on Cu(001) 300 K for two different deposition rates of (a) 2.0 min ML\(^{-1}\), and (b) 16.0 min ML\(^{-1}\), the fastest and slowest rates used in the experimental work vs. Fe coverage. Note that the abscissa is calibrated in ML. The majority of the deposition rates quoted in the literature are encompassed in this range. In both cases we observe strong, regular intensity oscillations as a function of Fe deposition time.

The critical film thickness achieved before relaxation to the bcc Fe phase by the change in oscillation amplitude, was relatively unaffected by the deposition rate, occurring after about 12 ML in both cases. The residual background contamination inherent in the vacuum environment appears to play no significant role during film growth at the working pressures of the experiment (5\times10^{-10} mbar). The effect of the prolonged exposure of a Fe surface to residual vacuum contaminants is considered in Section 5.4.7.

Although deposition at a faster rate suffered from poorer statistics a difference in the growth behaviour was evident. In Figure 5.12(a) the initial growth resembles the situation where no Fe-Cu intermixing takes place at the Fe-Cu interface during initial layer formation because the intensity of the oscillation corresponding to 1 ML coverage is lower than at 2 ML (compare with Figure 5.6). This implies that the Fe-Cu intermixing mechanism is dependent on deposition rate, as well as substrate temperature. One explanation may be that the faster deposition rate, by increasing the number of Fe atoms at the Cu surface, raises the probability of the arriving Fe atoms interacting with other adatoms to form Fe islands, and reducing the opportunity for atomic exchange with the Cu substrate ultimately decreasing the extent of intermixing.

5.4.6 Relaxation to the bcc Fe Phase

With increasing Fe film thickness, the difference in energy between the strained fcc Fe structure and the relaxed bcc phase grows. Eventually this will exceed the energy required to introduce defects and the structure will relax to the lower energy bcc Fe
Figure 5.12  The growth of Fe on Cu(001) 300 K for two different deposition rates of (a) 2.0 minutes ML\(^{-1}\), and (b) 16.0 minutes ML\(^{-1}\) plotted against Fe coverage in ML. The curves have been normalised to the clean Cu(001) specular intensity, and offset vertically for clarity. The Fe shutter was opened at t=0 minutes.
arrangement. In order to observe this relaxation measurements of inplane peaks were made, for example, around the \((2, 0, 0.16)\) peak from the Cu\((001)\) substrate. Scattering from the pseudomorphic fcc Fe phase will coincide with the scattering from the bulk, however, relaxation of the fcc structure will manifest itself as satellite peaks around the \((2, 0)\) inplane peak. In such a way it is possible to determine the structures formed upon epitaxial breakdown. Surprisingly, there is little experimental confirmation of the formation of the bcc structure. STM and LEED measurements by Wuttig et al (1993) suggested that above a coverage of 11 ML Fe grows in the bcc phase with the \((110)\) bulk orientation parallel to the surface. Magnan et al (1991) reported that upon relaxation to the bcc Fe phase even the first Fe layers at the Fe-Cu interface reordered when the thickness of the film increased. The exact coverage at which this relaxation occurs is dependent on the growth conditions.

We note that in Figure 5.2 there is a reduction in the measured amplitude at 13 ML which we attribute to the breakdown of epitaxy and formation of the bcc Fe phase. A radial scan along the \(<1\overline{1}0>\) axis after the deposition of 15 ML of Fe on Cu\((001)\) at 300 K revealed features which could be correlated with domains of bcc iron oriented with either the \((001)\) or the \((110)\) planes parallel to the \((001)\) surface of copper, see Figure 5.13, at values of \(h\) equals 1.78 and 2.19 rlu respectively (where \(h\) is the Miller index). The arrows on Figure 5.13 indicate the position where we would expect the diffraction peaks to occur if the bcc structures were completely relaxed. The inset diagrams illustrate the relationship between the bcc Fe phases and the Cu\((001)\) substrate (direct epitaxy of the bcc phase on the Cu\((001)\) face is not implied).

The bcc Fe phases induced maxima along fractional order diffraction rods at reciprocal lattice positions of \((0.9, 0.9, \ell)\) and \((1.07, 0, \ell)\) corresponding to the bcc Fe\((100)\) and bcc Fe\((110)\) phases respectively (Figure 5.14). The position and FWHM along \(\ell\) of the bcc Fe peaks provides information on the island thickness and relaxation. The experimentally measured FWHMs indicted that there was 5.9 layers of Fe\((001)\) and 7.66 layers of bcc Fe\((110)\) at a coverage of 15 ML. Calculating the FWHM expected from a bcc Fe structure as a function of thickness gives best agreement for values of 7 and 12 monolayers of Fe respectively. The arrows indicate the expected position of the Bragg peaks for a completely relaxed bcc structure.
Figure 5.13  (a) Transverse scan through the (2, 0, 0.15) peak after deposition of 15 ML of Fe on Cu(001) at 300 K. The features correspond with domains of bcc iron oriented with either the (001) or the (110) planes parallel to the (001) surface of copper. The inset diagrams illustrate the relationship between the bcc Fe phases and the Cu(001) substrate (direct epitaxy of the bcc phase on the Cu(001) face is not implied). The arrows indicate the position where we would expect the diffraction peaks to occur if the bcc structures were completely relaxed, (b) summarises the observations made in reciprocal space for this figure and Figure 5.14.
Figure 5.14  Bragg peaks induced at (a) (0.9, 0, 1.11) and (b) (1.07, 0, 0.9) for bcc Fe(100) and bcc Fe(110) respectively (the arrow indicates the expected position of the Bragg peaks for a completely relaxed bcc structure).
5.4.7 The Effect of Residual Contamination on Overlayer Relaxation

It has been reported for a number of experimental systems (Mozley et al. 1995, Johnson et al. 1993) that the presence of contaminant gases (mainly CO and O₂) at the sample surface can significantly modify the overlayer growth mode and surface morphology during vacuum deposition. The effect of the adsorbed gases is to create nucleation sites which aids mass transfer between layers. Adsorbed gases may cause step crossing.

As previously discussed, relaxation of the metastable fcc to bcc Fe phase occurs at a coverage around 13 ML, a figure generally agreed on in the literature, for an Fe film grown in a single deposition. When the total deposition is an accumulation of a number of shorter depositions over a period of time upon previously grown Fe surface then the overlayer growth behaviour is modified. In such a way the layer-by-layer growth of Fe on Cu(001) at 300 K was extended up to a coverage of 33 ML before breakdown of epitaxy was observed, illustrated in Figure 5.15 which shows a growth curve made up of 21 individual depositions over a period of time (the Knudsen cell was held at a constant temperature during this period). The as-deposited surface accumulated gaseous species from the vacuum environment promoting extended layer-by-layer film formation. The evolution of the bcc Fe structure was monitored with Fe coverage during the above deposition. The bcc Fe(001) phase appeared first. Over a coverage of 28 to 33 ML the Fe(001) satellite position relaxes by 1.1% in-plane and the (110) bcc peak by 0.5% relaxes in-plane towards the predicted positions.

A similarly improved layerwise growth mode was observed for the growth of Gd/Mo(110) attributed to the formation of nucleation sites to aid the mass transport between layers (Mozley et al. 1995). The effect of allowing the surface to reach an equilibrium state may also play a role in the growth mechanism (epitaxy is a non-equilibrium process). CO may act as a surfactant by reducing surface energy barriers or providing nucleation sites (van der Vegt 1995).

In summary, residual contamination from the vacuum (mainly CO) at the metal surface promoted layer formation over an extended coverage range and delayed relaxation of the overlayer to the bcc phase.
Figure 5.15  Growth of Fe on Cu(001) in stages of 1, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18, 20, 24, 28, 33, and 38 ML depositions.
5.5 Conclusions

Epitaxial growth was employed to stabilise the metastable fcc phase of Fe at room temperature. The overlayer growth mode had a strong dependence on the substrate temperature during deposition. At 85 K growth was diffusion limited. Growth at elevated temperatures eventually become dominated by the effects of increased Fe-Cu interdiffusion and poor layer formation ensued.

SXRD measurements clearly showed that the growth mode of Fe on Cu(001) at 300 K to be in a Frank van der Merwe (layer-by-layer) mechanism up to about 13 ML with limited atomic Fe-Cu exchange at the interface of the two metals. Other growth modes can be excluded. A bilayer growth mode was ruled out after measurements as a function of perpendicular momentum transfer. Intermixing was confirmed in the first subsurface layer and first Fe monolayer, with Fe included in equal amounts in the two layers. Initial investigations suggested that the extent of Fe-Cu intermixing at 300 K had a dependence the Fe deposition rate.

Quantitative analysis of the specular reflectivity measured as a function of deposition time determine the layer heights of a 2 ML thick Fe film to be 1.71±0.1 and 3.54±0.1 Å above the substrate. Only limited information is gained from the above analysis as only one point in reciprocal space is monitored as a function of time. A more accurate analysis of the out of plane structure is presented in the next chapter.

Relaxation of the metastable fcc Fe phase to the bulk bcc phase occurred at a coverage of about 13 ML and evidence was found for well-established bcc (100) and bcc (110) Fe structures.

The effect of adsorbed gases at the surface was to promote extended layer growth and delay relaxation to the bcc Fe phase.
Chapter 6

The Atomic Structure of Fe on Cu(001)

6.1 Summary

The pseudomorphic growth of fcc Fe layers on Cu(001), prepared by MBE, was described in Chapter 5. The subsequent film structure at 300 K is reported in this chapter. This is the first investigation to include Fe-Cu atomic intermixing at the adsorbate-overlayer interface in the structural analysis. In the analysis, atoms were exchanged between substitutional positions in the topmost copper layer and first Fe adlayer, improving the fits to the data. The structure of the clean Cu(001) and adsorbate-covered surfaces, at coverages of 1, 2, 4, and 6 monolayers (ML), were determined from intensity measurements normal to the sample surface (rod scans). The magnetic behaviour of the films is intrinsically linked to the atomic structure and a detailed knowledge of the latter is required to fully characterise the former.

The clean Cu(001) surface exhibited multilayer relaxation with a contraction of the top copper interlayer spacing of 1.55%, accompanied by a slight expansion of the next interlayer spacing by 0.13%, in good agreement with previous work (Lind et al.).

In the analysis of the clean substrate and adsorbate-covered surfaces the top two layers of the structure in question were allowed to relax. On Fe deposition a significant increase in the surface roughness was observed. At an Fe coverage of 1 ML the surface interlayer spacings were 1.85 Å and 1.70 Å for the Fe adlayer and first subsurface layer respectively. The d-spacing of the Fe adlayer was considerably expanded in comparison to its bulk value (1.77 Å). At 2 ML Fe coverage the surface roughness was much reduced. Both Fe layers exhibited an expansion (to 1.85 Å). Expansion of the topmost interlayer spacing at the surface of the Fe film reached a maximum at a coverage of 4 ML (to 1.86 Å). The surface roughness was high, possibly due to the formation of a dislocation network that preempts the collapse to the bcc Fe phase. At a 6 ML coverage the Fe overlayer structure was close to that of bulk fcc Fe(001), except for an expansion of the topmost interlayer spacing at the surface of the film.

Suggestions are put forward to explain contradictory results in the literature between different analytical techniques based on the SXRD results in this chapter.
6.2 Background

In the previous chapter a study of particular aspects of the growth of fcc Fe overlayer on the Cu(001) surface, prepared by MBE, was presented. This chapter investigates the resulting overlayer structure at 300 K and its dependence on film thickness. Changes in the interlayer spacing can be correlated with the observed unusual magnetic behaviour of the Fe/Cu(001) system (Clarke et al 1987). A review of literature relating the structure of Fe films on Cu(001) to the magnetic behaviour of the film is first given emphasising the link between the structural and magnetic behaviour.

When a bulk metal crystal is terminated by a surface the atomic co-ordination and electron distribution is altered and the surface possesses a different crystallography to that of the bulk. Multilayer relaxation is common at the surface of metals and involves a redistribution of the truncated electron density in order to accommodate atoms in a lower energy configuration. For an (001) close-packed metal structure we expect only small perpendicular relaxations at the surface. From embedded atom calculations (Dobson 1988) it was found that the Cu crystal prefers a smaller unit cell for its free standing surface than in the bulk, and, even though the relatively large mismatch gives a strain in the Cu surface plane, the process is more favourable than inducing surface reconstruction.

The bulk interlayer spacings expected for epitaxially strained fcc Fe(001) and bcc Fe(001) films on Cu(001), calculated by Jona and Marcus (1989), are 1.77 Å and 1.65 Å respectively, assuming an inplane lattice constant of 2.55 Å. Metal adatoms deposited on oriented metal surfaces, however, will not necessarily form simple adlayers and the quality and (magnetic) properties of an epitaxial film depend on many factors. Novel magnetic behaviour in the films is strongly related to the details of the film structure. The epitaxially grown fcc Fe phase is subject to strain and this distortion can induce novel magnetic states (Dongqi Li et al 1994). Measured magnetic anisotropies are attributed to the interlayer expansion (Clarke et al 1987).

Changes in the magnetic behaviour of Fe on Cu(001), from uniform magnetisation to surface magnetism, have been observed in the 4 to 5 ML range and a change from perpendicular to inplane magnetisation at a coverage of 11 ML (Thomassen et al 1992). In the coverage regime from 5-11 ML Fe films were essentially (Cu) bulk-like in structure with slightly contracted interlayer spacing in the film with an expanded surface layer (Darici et al 1987, Lu et al 1989, Wuttig and Thomassen 1993). The expanded interlayer spacing at the film surface was correlated with the observation of ferromagnetic coupling.
Figure 6.1 The magnetic phase diagram of Fe as a function of temperature and thickness. In region I the films are ferromagnetic with perpendicular easy axes. In region II(a) the surface is ferromagnetic, the underlying layers anti-ferromagnetic. In region II(b) the films are ferromagnetic with inplane easy axes. In region III the films are ferromagnetic with inplane easy axes. (after Dongqi et al 1994).
Structural studies of 8 and 11 ML thick films of Fe on Cu(001), investigated by Wuttig et al. (1993), indicated a strained, distorted fcc lattice (lattice parameters of 3.61 Å and 3.54 Å) with an expanded first interlayer spacing (~0.1 Å). The results confirmed the work of Lu et al. (1989) and Landskron et al. (1991). Giergiel et al. (1994) observed a slight relaxation of the film at a coverages from 6 to 8 ML and identified nucleation sites at a coverage as low as 4.6 ML which initiated the development of a stress relieving network within the film. Clarke et al. (1987) investigated the evolution of the Fe film from 1 to 7 ML using LFFDI-V showing the interlayer spacings to vary with Fe coverage. An anti-ferromagnetic state was associated with a well-defined fcc structure, whereas the ferromagnetic phase was induced by a distorted structure. Kraft et al. (1994) performed extensive total energy calculations, investigating different types of intralayer and interlayer magnetism, to determine the atomic and magnetic structure of the Fe films on Cu(001). The authors concluded that the surface and subsurface layers couple ferromagnetically whereas the deeper layers show antiferromagnetic coupling. The first interlayer expansion was 3.9% accompanied by a 1% contraction of the second layer d-spacing.

6.3 Results

The vertical morphology of the clean Cu(001) and Fe-covered surfaces was determined from the kinematical analysis of rod scan data, that is, intensity measurements perpendicular to the substrate surface as a function of perpendicular momentum transfer (q) made at integer order (hk) positions in reciprocal space. The crystal truncation rods contain information about areas of ordered lateral structure at the surface. The (10l) and (11l) crystal truncation rods were recorded. Specular reflectivity data (h=0, k=0, l) was inconsistent with the above data since the specular scattering originates from both areas of order and disorder at the surface. Fe coverages of 1, 2, 4, and 6 ML were investigated. Fe was deposited on a freshly prepared clean Cu(001) surface in each case under the same growth conditions.

The quality of the proposed structural model was determined from comparing theoretical structure factor amplitudes with the measured values by calculating the reduced chi-squared, χ² (see Section 4.5.2). The goodness of fit was given by the reduced χ² value. (the error analysis has been put in the summary table, Table 6.6, at the end of the chapter so as not to confuse the text). A scale factor, to allow for the experimental geometry, was determined from the clean surface and fixed during analysis of all surfaces. A roughness parameter (Robinson 1986) was included in the fitting procedure to account for the surface roughness. It is convenient to express the surface roughness as the root-mean-square elevation of the surface contour, σrms, in Å. The lattice positions of specific crystal layers were allowed to relax perpendicular to the surface in order to derive the exact atomic structure.
A schematic diagram of the model used in the structural analysis is given in Figure 6.2. This figure also indicates the notation assigned to each interlayer spacing. The magnitude of the topmost interlayer spacings of the bulk Cu lattice are denoted by \( d_{\text{Cu1}}, d_{\text{Cu2}} \) and \( d_{\text{Cu3}} \) respectively (in Å) and the change in interlayer spacing by \( \Delta d_{\text{Cu1}}, \) etc., as a percentage of the bulk copper lattice parameter (3.615 Å). From the top of the substrate upwards the d-spacings of the deposited Fe layers are denoted by \( d_{\text{Fe1}}, d_{\text{Fe2}}, \) etc. The occupancy of all layers was fixed at 100%. In reality the Fe-Cu interface is not a sharp elemental break and it has previously been shown (see Chapter 5) that atomic intermixing occurs at the overlayer-substrate interface when Fe is deposited on Cu(001). The intermixing is confined to the two layers indicated in the diagram: the topmost substrate layer and the first Fe adlayer.

### 6.3.1 The Clean Cu(001) Surface

It is important to consider the possibility of multilayer relaxation when performing surface crystallography. The clean Cu(001) surface has been extensively studied in the past and exhibits small multilayer relaxations alternating in sign with no reconstruction of the surface. Thus, we have a well-characterised surface on which to test the validity of the analytical procedure.

Pendry (1974) theoretically investigated the multilayer relaxations at the Cu(001) surface predicting the interlayer spacing at the surface \( d_{\text{Cu1}} \) to be greater than the bulk Cu interlayer spacing, \( d_{\text{bulk}} = 1.81 \) Å. However, studies reported contradictory results (Jona 1978) and, for low index metals in general, it was experimentally found that \( d_{\text{Cu1}} \) was less than \( d_{\text{bulk}} \). The discrepancy between experiment and theory was resolved by considering the modification of the conduction electron distribution that occurs producing smoothing of the electronic charge density which lowers the kinetic energy parallel to the surface, accompanied by a force constant stiffening (Smoluchowski 1941, Finnis and Heine 1974).

Figure 6.3(a) shows the model used in fitting the clean Cu(001) data. The model is derived from Figure 6.2 by removing all layers above the layer Cu1, indicated by the dashed line. Obviously there is no intermixing for the clean surface since Fe has not been deposited and the composition of all layers is pure copper. In Figure 6.3(a) the size of the interlayer spacings \( (d_{\text{Cu1}}, d_{\text{Cu2}}) \) is given (in Å) along with the overall change magnitude and direction \( (\Delta d_{\text{Cu1}}, \Delta d_{\text{Cu2}}) \) of the interlayer spacing compared with bulk copper lattice (i.e. as a percentage of the copper lattice parameter, \( a_0 = 3.615 \) Å). Figure 6.3(b) shows the measured data for the (10\( \ell \)) and (11\( \ell \)) rod scans, plotted
Figure 6.2  Schematic model of Fe on Cu(001) overlayer structure showing the nomenclature used in the text. The units of the d-spacings are Å. The dashed line indicates the top of the original bulk Cu lattice. Intermixing occurs at the overlayer-substrate interface and in confined to the two interfacial layers as indicated.
as a function of structure factor vs. perpendicular momentum transfer, \( t \). The solid line is the best fit to the measured data for the model described in the text, the dotted line indicates the structure factor for the bulk terminated Cu(001) surface, i.e. with no relaxation of the layers. To illustrate the sensitivity of the SXRD measurements simulations were performed in which the position of the top layer of the substrate only was allowed to relax by \( \Delta d_{\text{Cu1}}=\pm 4\% \) (dash-dot line and dashed line respectively). The difference between the two situations is quite marked confirming the sensitivity of the measurements to relaxation on an atomic level.

On truncation of the bulk Cu(001) crystal an oscillatory relaxation of the interlayer spacings was detected at the surface region. From the SXRD measurements, the interlayer spacing of the topmost Cu layer was contracted by 1.55\( \pm \)0.5\% (\( \Delta d_{\text{Cu1}} \)), accompanied by an expansion of 0.13\( \pm \)0.4\% (\( \Delta d_{\text{Cu2}} \)) for the next deepest layer with a best fit reduced \( \chi^2 \) of 0.92. All other atomic layers were fixed at the (Cu) bulk lattice positions, as illustrated in Figure 6.3(a). The results are consistent with an oscillatory layer relaxation which decreases in magnitude with the depth below the surface. The clean Cu(001) surface had an rms roughness of 0.17 \( \AA \). The roughness values obtained in the analysis were in good agreement with those determined by Robinson (1986) for metal surfaces.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Technique</th>
<th>( \Delta d_{\text{Cu1}} ) (%)</th>
<th>( \Delta d_{\text{Cu2}} ) (%)</th>
<th>( \Delta d_{\text{Cu3}} ) (%)</th>
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<td>+2.25</td>
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<td>+1.7( \pm )0.6</td>
<td>+1( \pm )2</td>
</tr>
<tr>
<td>Abu-Joudeh et al (1986)</td>
<td>LEED</td>
<td>-2</td>
<td>+1.5</td>
<td></td>
</tr>
<tr>
<td>Alkemade et al (1986)</td>
<td>MEIS</td>
<td>-2( \pm )2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lind et al (1987)</td>
<td>SPLEED</td>
<td>-1.2</td>
<td>+0.9</td>
<td></td>
</tr>
<tr>
<td>Jiang et al (1991)</td>
<td>MEIS</td>
<td>-2.4( \pm )0.8</td>
<td>+1.0( \pm )1.0</td>
<td></td>
</tr>
<tr>
<td>Mizuno et al (1993)</td>
<td>LEED</td>
<td>-7( \pm )3</td>
<td>+2( \pm )4</td>
<td></td>
</tr>
<tr>
<td>Folies et al (1986)</td>
<td>Theory</td>
<td>-1.4</td>
<td>-0.3</td>
<td></td>
</tr>
<tr>
<td>James et al (1995)</td>
<td>SXRD</td>
<td>-1.55( \pm )0.5</td>
<td>+0.13( \pm )0.4</td>
<td></td>
</tr>
</tbody>
</table>

*Table 6.1  Summary of experimental and theoretical studies of Cu(001) surface relaxation*

Experimental studies of Cu(001) surface relaxation have been performed using numerous techniques, including LEED, LEED I-V analysis, SPLEED, EELS, AES, and ARPES, as summarised in Table 6.1 above (including references). The results are
Original Cu Bulk

\[ \begin{align*}
    d_{Cu1} &= 1.75 \text{ Å} \quad \Delta d_{Cu1} = -1.55\% \\
    d_{Cu2} &= 1.81 \text{ Å} \quad \Delta d_{Cu2} = +0.13 \% \\
    d_{bulk (Cu)} &= 1.81 \text{ Å}
\end{align*} \]

**Figure 6.3** (a) Schematic model of clean Cu(001) atomic structure

... /continued
Figure 6.3  (b) (10£) and (11£) rod scans for the clean Cu(001) surface. Also illustrated is the sensitivity of SXRD to atomic layer relaxation for the cases where the topmost substrate layer was relaxed by ±4 % (dash-dot line and dashed line respectively).
generally in good agreement with previous work indicating the validity of the approach. The results of Lind et al (1987), using SLEED, are best supported by the SXRD data.

In summary, the clean Cu(001) surface shows an oscillatory behaviour in the multilayer relaxation at the surface, as expected, with the top layer expansion greater than that of the next deepest layer. The roughness of the surface is low at a value of 0.17 Å (σrms). The results for the clean surface give justification for allowing the top two layers to be freed in the analysis, the procedure which will be followed from this point onwards. Allowing only the top Cu layer to relax produced a contraction of the interlayer spacing of 1.53% with a χ^2 of 0.92. The rms roughness was 0.17 Å. Including the top three layers of the Cu(001) surface as free parameters in the fitting procedure did not give any significant improvements.

6.3.2 1 ML of Fe on Cu(001)

Fe-Cu Atomic Intermixing

During the deposition of Fe on Cu(001) intermixing of the substrate and overlayer atoms occurs at the interface, as shown in Chapter 5. To simulate Fe-Cu intermixing at the adsorbate-substrate interface the topmost substrate layer substitutionally included a proportion of the deposited Fe atoms, ejecting Cu atoms from the substrate which were incorporated into the first Fe monolayer. A crude estimate of the extent of intermixing was determined from the 300 K growth curve, giving a value of x=0.35 (x was defined in Chapter 5 as the fraction of Fe incorporated into the substrate, 0<x<1), i.e. the top substrate layer contained 35% intermixed Fe. The value generally quoted in the literature is x=0.5, i.e. Fe is included in equal proportions in the first Fe layer and first subsurface layer (see, for example, Detzel et al 1993 and Johnson et al 1994). The amount of intermixing can be verified from the analysis of the measured data presented in this chapter. The computer software did not allow a sophisticated analysis of the intermixing phenomenon, however, values of 0%, 35% and 50% intermixing were tested on the measured data. The results for a 1 ML overlayer are presented in the table below, where two layers are relaxed (Table 6.2).

Inspecting Table 6.2, which gives the effect of intermixing on the reduced χ^2, the rms roughness and the change in layer spacings for the two freed layers (dCu1 and dFe1), we find that a surface with no intermixing gives a significantly worse χ^2 value than when intermixing is included. The effect is quite dramatic and clearly confirms that the top substrate and first monolayer are intermixed to some extent. A small improvement in the χ^2 value is observed for x=0.5 compared to x=0.35. In the
following analysis of the Fe-covered surfaces the intermixing was fixed at x=0.5 at all coverages.

<table>
<thead>
<tr>
<th>Intermixing</th>
<th>x=0.0 (0&lt;x&lt;1)</th>
<th>x=0.35</th>
<th>x=0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^2$</td>
<td>5.56</td>
<td>4.42</td>
<td>4.14</td>
</tr>
<tr>
<td>rms roughness (Å)</td>
<td>0.98±0.03</td>
<td>1.12±0.03</td>
<td>1.20±0.03</td>
</tr>
<tr>
<td>$\Delta d_{Cu}$ (Å)</td>
<td>1.69±0.02</td>
<td>1.70±0.02</td>
<td>1.70±0.02</td>
</tr>
<tr>
<td>$\Delta d_{Fe}$ (Å)</td>
<td>1.88±0.02</td>
<td>1.86±0.02</td>
<td>1.85±0.02</td>
</tr>
</tbody>
</table>

Table 6.2 Compare the effects of intermixing at a coverage of 1 ML Fe on Cu(001) for intermixing of x=0, 0.35, and 0.5, on the reduced $\chi^2$, the rms roughness, and the change in layer spacings for the top two layers.

1 ML of Fe on Cu(001)

Fe was deposited on the Cu(001) surface at 300 K up to a coverage of 1.0±0.05 ML, calibrated by following the evolution of the x-ray specular reflectivity at (0, 0, 1.0) during deposition, as described in Chapter 5. From the above, Fe-Cu atomic intermixing at the adsorbate-substrate interface was included in the analysis at x=0.5. The intermixing was confined to the topmost substrate layer and the first Fe adlayer, with Cu and Fe atoms randomly occupying fcc positions in the intermixed region. The in-plane lattice parameter of the fcc Fe film was fixed at the bulk substrate value (2.55 Å) and not adjusted in the analysis. Müller et al (1995) varied the in-plane lattice constant of the Fe overlayer during the analysis, but found that the parameter had little effect on the results. They concluded that the data was ultimately dominated by the vertical spacings and the value of the in-plane parameter had a minimal influence on the results.

Figure 6.4(a) shows the model used in the analysis of 1 ML of Fe on Cu(001). The topmost substrate layer is considered a perfect continuation of the bulk Cu lattice ($d_{bulk}(Cu)=1.81$ Å) at the start of analysis. The deposited Fe monolayer is initially placed at a height consistent with the interlayer spacing of the Fe(001) structure when epitaxially matched to the Cu(001) surface ($d_{bulk}(fcc Fe)=1.77$ Å, referred to as $d_{bulk}(Fe)$ here afterwards since we are discussing the fcc phase), described earlier in the text. So, initially we have a bulk terminated Cu(001) surface with an Fe layer at a height of 1.77 Å and it is from these positions that the layers are freed in the analysis. Reasonable alternative starting positions do not affect the outcome of the analysis. Note that in Figure 6.4(a) $\Delta d_{Cu}$ is referenced to $\Delta d_{bulk}(Cu)$ and $d_{Fe}$ to $d_{bulk}(Fe)$.

On deposition of 1 ML of Fe on the Cu(001) surface a dramatic increase in the surface roughness was observed. We observed an expansion in the Fe adlayer interlayer
Figure 6.4  (a) Schematic model of the atomic structure of 1 ML Fe on Cu(001)

\[ d = 1.85 \, \text{Å} \quad \Delta d_{\text{Fe}1} = +2.21\% \]
\[ d = 1.70 \, \text{Å} \quad \Delta d_{\text{Cu}1} = -3.11\% \]
\[ d_{\text{bulk}}(\text{Cu}) = 1.81 \, \text{Å} \]

\[ ^{+}\text{wrt } d_{\text{bulk}}(\text{Fe}) = 1.77 \, \text{Å} \]
\[ ^{*}\text{wrt } d_{\text{bulk}}(\text{Cu}) = 1.81 \, \text{Å} \]
Figure 6.4  (b) (10f) and (11f) rod scans for 1 ML of Fe on Cu(001) with the best fit (solid line) described in the text.
spacing ($d_{Fe}=1.85 \text{ Å}$) together with a contraction of the first subsurface interlayer spacing ($d_{Cu}=1.70 \text{ Å}$), with a poor reduced $\chi^2$ of 4.14. The roughness was considerably higher than the case of the clean Cu(001) surface at 1.20 Å. In Figure 6.4(b) the (100) and (110) rod scans for 1 ML of Fe on Cu(001) are displayed along the best fit described above (solid line). The dotted line is the structure factor calculated for the bulk terminated substrate. The $\chi^2$ value is by no means satisfactory, however, the poor fit to the measured data indicates that the film morphology is complex and the Fe adatoms do not simply form a flat adlayer. On Fe deposition the metal surface was considerably roughened.

In the analysis the intermixed layers, consisting of Cu and Fe atoms occupying random lattice sites within an fcc structure, were relaxed as a single, integral unit, i.e. the Cu and Fe atoms had the same displacement during layer relaxation. If the Cu and Fe atoms are independently allowed to relax within the intermixed layer, however, a buckling of the overlayer is observed, with the Fe atoms sitting below the slightly raised Cu atoms in the intermixed film, giving a relative displacement of about 0.4 Å and a slightly improved $\chi^2$. The exact nature of the buckling can not be confidently predicted from the present data due to the statistical uncertainty in increasing the number of free parameters. A buckling of the overlayer is not unfeasible and may be the underlying process behind the observation of surface reconstruction in Fe films reported by certain authors (see, for example, Thomassen et al 1992). The Fe overlayer showed no evidence of reconstruction in this work.

In summary, Fe deposition on Cu(001) at 300 K to a coverage of 1 ML caused a dramatic change in the surface morphology, with a substantial increase in the surface disorder. Fe-Cu intermixing ($x=0.5$) at the interface was shown to occur. A contraction of the interlayer spacing at the surface was observed. A poor fit to the measured data indicated that the overlayer morphology was actually quite complex.

### 6.3.3 2 ML of Fe on Cu(001)

A model for a 2 ML thick overlayer of Fe on Cu(001) is presented in Figure 6.5(a). The Cu(001) substrate was terminated by an intermixed Fe-Cu layer and the first Fe adlayer was also intermixed, as previously described. The intermixing was confined to the two interfacial layers and therefore the second Fe monolayer did not contain out-diffused substrate atoms. The d-spacing of the Fe overlayer was taken to be the bulk d-spacing, $d_{bulk}(Fe)$, as a starting point in the analysis. The substrate layers were not allowed to relax in the analysis and only the topmost two layers were freed, in accord with previous analysis conditions.
Figure 6.5 (a) Schematic model of the atomic structure of 2 ML of Fe on Cu(001)

\[ d_{Fe2} = 1.85 \, \text{Å} \quad \Delta d_{Fe2} = +2.27\% \]
\[ d_{Fe1} = 1.85 \, \text{Å} \quad \Delta d_{Fe1} = +2.26\% \]
\[ d_{bulk(Cu)} = 1.81 \, \text{Å} \]
Figure 6.5  (b) (10\text{f}) and (11\text{f}) rod scans for 2 ML of Fe on Cu(O01).

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The results for 2 ML of Fe on Cu(001) are summarised schematically in Figure 6.5(a). Both the topmost Fe layers expanded by about 2.26%, giving a d-spacing for $d_{\text{pe}1}$ and $d_{\text{pe}2}$ of 1.85 Å. Figure 6.5 shows the measured rod scans with the fit to the data. The rms roughness was 0.42 Å with an overall reduced $\chi^2$ of 0.41. The value of the roughness at 2 ML is a third of that for the 1 ML film. The small $\chi^2$ value suggests a statistical instability in the analysis of this film, but for consistency we have relaxed the top two layers.

The results implied that as the coverage increased from 1 to 2 ML the disordered overlayer accepted Fe adatoms at preferential sites to till in the film and by a coverage of 2 ML the film consisted of comparatively well-ordered Fe adlayers indicating a change in the layer filling behaviour with film thickness.

It is possible that interpretation of this complex growth behaviour varies between different analytical techniques. A particular technique only measures limited aspects of the real system and a number of techniques should be combined to obtain an accurate description. The high roughness in the initial stages of overlayer formation may appear as Fe agglomeration when measured by, for example, helium atom scattering (HAS), which is very sensitive to surface disorder. Dastoor et al (1992) observed a sharp drop in HAS specular intensity during initial growth indicating a high density of defects at the surface, in agreement with this study. Suggestions of a bilayer growth mode at the start of deposition may arise as a consequence of the intermixing mechanism in which two intermixed layers effectively form at the same time. The final result may appear like homoepitaxial growth of an Fe-Cu film upon an Fe-Cu layer (if $x=0.5$). The above may explain some of the results observed by other authors.

### 6.3.4 4 ML of Fe on Cu(001)

The experimentally measured rod scans and structural model for 4 ML of Fe on Cu(001) are presented in Figure 6.6. By a coverage of 4 ML a 3D Fe film was established with a bulk d-spacing of 1.77 Å. The upper two Fe layers of the film were allowed to relax in the analysis. The best fit is displayed in Figure 6.6(b) and described below.

At a coverage of 4 ML the two surface layers exhibited a significant interlayer expansion, with $d_{\text{pe}4}=1.86$ Å and $\Delta d_{\text{pe}3}=1.81$ Å, as illustrated in Figure 6.6(a). The reduced $\chi^2$ was 3.34 and a large rms roughness of 1.05 Å was observed.

The rms roughness had significantly increased again at this stage of film development and perhaps indicated structural changes within the film, for example,
Figure 6.6 (a) Schematic model of the atomic structure 4 ML of Fe on Cu(001)
Figure 6.6 (b) (10\ell) and (11\ell) rod scans for 4 ML of Fe on Cu(001).
the formation of a dislocation network that preempts the collapse to the bcc Fe phase, reported to begin at coverages as low as about 4.6 ML (Giergiel et al 1994). It would appear that expansion in the adlayers causes considerable disruption of the film structure. The overlayer expansion can be correlated with unusual magnetic effects associated with fcc Fe films at around the same coverage (Pescia 1987, Bland 1987). The structural changes in the film over a coverage from 1-5 ML may induce the observed novel magnetic behaviour.

6.3.5 6 ML of Fe on Cu(001)

6 ML of Fe were deposited on a freshly prepared Cu(001) surface at 300 K. The overlayer structure is schematically represented in Figure 6.7(a) and the rod scans showing the best fit to the measured data given in Figure 6.7(b). The majority of the film is held at the anticipated bulk value for fcc Fe (1.77 Å) with the upper two layers relaxed in the analysis.

The surface Fe layers still exhibit interlayer expansion at a 6 ML coverage, but to a lesser extent than in the 4 ML case. From the analysis $d_{6f}=1.85$ Å and $d_{6f0}=1.79$ Å, the roughness was reduced to 0.65 Å, with a $\chi^2$ of 2.62 (Figure 6.5(b)). The SXRD results are compared with previous studies at a coverage of 6 ML in Table 6.3 below. The table lists the three topmost interlayer spacings (in Å), where measured, for 6 ML of Fe on Cu(001) by the authors indicated. General agreement of the SXRD data is seen with the more recent studies. The expansion of the top layer is in good agreement with the other studies. The bulk of the Fe overlayer is significantly expanded in the study by Clarke et al (1987), but this was not observed in the other studies.

<table>
<thead>
<tr>
<th>Fe coverage</th>
<th>$d_{6f}$ (Å)</th>
<th>$d_{6f0}$ (Å)</th>
<th>$d_{6f0}$ (Å)</th>
<th>$d_{bulk}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 ML Clarke et al (1987)</td>
<td>1.84±0.02</td>
<td>1.84±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 ML Landskron et al (1991) a)</td>
<td>1.88±0.02</td>
<td>1.81±0.03</td>
<td>1.77±0.02</td>
<td></td>
</tr>
<tr>
<td>6 ML Müller et al (1995) b)</td>
<td>1.87±0.011</td>
<td>1.78±0.012</td>
<td>1.76±0.02</td>
<td>1.78±0.02</td>
</tr>
<tr>
<td>6 ML James et al (1995) c)</td>
<td>1.85±0.02</td>
<td>1.79±0.02</td>
<td>1.77</td>
<td>1.77</td>
</tr>
</tbody>
</table>

Table 6.3 Compilation of authors' results for the structure of 6 ML of Fe on Cu(001). a) performed at 90 K, b) inplane lattice parameter, $a_{ip}$, is 2.52±0.015 Å, c) structural model includes Fe-Cu atomic intermixing at the interface. Numbers in italics are not released in the fitting procedure.
Figure 6.7  (a) Schematic model of the atomic structure of 6 ML Fe on Cu(001) at 300 K
Figure 6.7 (b) (10\ell) and (11\ell) rod scans for 6 ML of Fe on Cu(001).
6.4 Conclusions

The structure of the clean Cu(001) shows multilayer relaxation in the two topmost layers and the results are in good agreement with previous work confirming the validity of the method used in this work.

The overlayer structure of fcc Fe films deposited on Cu(001) at 300 K evolved a function of Fe coverage. In particular, changes in the interlayer spacing at the film surface showed a dependence, in magnitude and direction, on the overlayer coverage. At the lowest coverage (1 ML) an expansion of the overlayer spacing was observed. The overlayer was very disordered. Fe-Cu intermixing at the overlayer-substrate interface was shown to occur from the analysis. This is the first study to include Fe-Cu intermixing at the interface in the structural analysis of the overlayer. With increasing Fe coverage the overlayer displayed an expansion in the interlayer spacings at the film surface, reaching a maximum at a 4 ML coverage. A high level of disorder at this coverage perhaps indicated the start of the film transformation to the bcc Fe phase. At 6 ML the overlayer was essentially a bulk fcc Fe film (d\text{bulk}(Fe)=1.77 Å) with the surface interlayer spacings expanded. A summary of the two outermost interlayer spacings (1st spacing and 2nd spacing) is given in Table 6.4, with rms roughness and the χ², and shown graphically in Figure 6.7. In the present analysis the intermixed top substrate was assumed to be a perfect extension of the Cu(001) bulk lattice, however, it is possible that the d-spacing at the intermixed region (d\text{Cu}) will be different from that of the Cu (and Fe). Setting the d-spacing d\text{Cu} to that of bulk Fe still gave agreement with the above analysis (within experimental error) showing expansion in the outer layers. The present data set is limited to two diffraction rods and a more comprehensive analysis requires the measurement of many more rods. Analysis based on a larger data set would allow refinement of the structural model.

There is strong link between the overlayer structure and the magnetic properties of fcc Fe films grown by MBE on Cu(001). Fe exists in several magnetic phases which have similar lattice constants near that of fcc Fe (3.615 Å), as previously shown in Figure 2.2. Consequently the magnetic behaviour is sensitive to the precise geometric structure. The dramatic changes observed in the magnetism of fcc Fe layers on Cu(001) with Fe coverage has been attributed to the interlayer expansion observed in the overlayer (Clarke et al 1987). The atomic structure of a surface is its most fundamental characteristic and the determination of any other properties must be based on a realistic geometrical model. A detailed knowledge of the exact film structure is paramount to understanding and controlling the novel magnetic behaviour of fcc Fe films.
Table 6.4 Summary of the two outermost interlayer spacings (1st spacing, 2nd spacing), rms roughness, and $\chi^2$ value as a function of overlayer coverage. Numbers in italics indicate parameters not released in the fitting procedure.

<table>
<thead>
<tr>
<th>Fe thickness /ML</th>
<th>1st spacing (Å)</th>
<th>2nd spacing (Å)</th>
<th>$\sigma_{rms}$ (Å)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>clean Cu(001)</td>
<td>1.75±0.02</td>
<td>1.81±0.02</td>
<td>0.17±0.12</td>
<td>0.92</td>
</tr>
<tr>
<td>1</td>
<td>1.85±0.02</td>
<td>1.70±0.02</td>
<td>1.20±0.03</td>
<td>4.14</td>
</tr>
<tr>
<td>2</td>
<td>1.85±0.02</td>
<td>1.85±0.02</td>
<td>0.42±0.02</td>
<td>0.41</td>
</tr>
<tr>
<td>4</td>
<td>1.86±0.02</td>
<td>1.81±0.02</td>
<td>1.05±0.03</td>
<td>3.34</td>
</tr>
<tr>
<td>6</td>
<td>1.85±0.02</td>
<td>1.79±0.02</td>
<td>0.65±0.21</td>
<td>2.62</td>
</tr>
</tbody>
</table>

bulk of Cu       | 1.81           | 1.81           |
bulk of Fe       | 1.77           | 1.77           |

Figure 6.8 Plot of the two outermost interlayer spacings (1st spacing, 2nd spacing) vs. Fe coverage. The bulk fcc Cu and bulk fcc Fe d-spacings are indicated on the diagram.
Chapter 7

The Growth of 3d Metals on the GaAs(001) Surface

7.1 Summary

This chapter reports on the epitaxial growth of transition metal films on GaAs(001). A brief study of the clean GaAs(001)4×1 surface is also presented. The room temperature growth mode, the interaction of the metal with the substrate, and the film structure are investigated. The effect of annealing an as-grown metal film is reported.

The amorphous-As (α-As) capped GaAs(001) surface was inhomogeneous after storage in air with crystallites of As₂O₃ at the surface, observed by scanning electron microscopy (SEM). After thermal desorption of the α-As cap a GaAs(001)4×1 reconstruction was observed, upon which metal deposition was performed.

Epitaxial growth was employed to induce formation of the non-equilibrium (metastable) bcc phase of Co on GaAs(001). This novel structure is of considerable interest. Overlayer growth proceeded in a three-dimensional (3D) manner accompanied by disruption of the substrate. The metal film included released substrate species, the concentration of which decayed exponentially from the metal-semiconductor interface and surface segregated species were detected. The structure of the film was consistent with the bcc Co phase. The hcp phase was observed on annealing a thick (50 ML) Co film to 773 K.

Deposition of Fe on GaAs(001) followed the same behaviour as Co. The growth and film structure were better defined and the extent of substrate disruption and intermixing were reduced.

7.2 Background

7.2.1 III-V Compound Semiconductors

Compound semiconductors are fundamentally different from their elemental counterparts since they possess an extra compositional degree of freedom in their stoichiometry. The area of III-V semiconductor research is a well established, far-reaching field encompassing fundamental investigation and technological
application. The research is motivated by a need to produce stable electrical contacts in electronic devices (Palmstrom and Morgan 1985).

The surface of a semiconductor is characterised by the atoms in the top layer, which have fewer nearest neighbours than the bulk atoms, resulting in different structural and electronic properties. An ideal termination of the bulk crystal would have surface atoms located at bulk lattice positions, but generally there is a high degree of free energy at the surface, associated with dangling bonds, and the surface region tends to reconstruct producing a surface unit cell with a different periodicity to the bulk, for example, the Si(111)7x7, Si(001)2×1, and GaAs(001)2×4 surfaces. For compound semiconductors the observed surface reconstructions have an additional dependence on the chemical composition at the surface.

The III-V semiconductor to receive the most attention over recent years is GaAs and the non-polar (110) surface, which does not exhibit a variable stoichiometry, is the most studied and understood crystal face. The (001) face, however, is technologically more important since most GaAs devices are epitaxially grown on this face. For the GaAs(001) surface, minimisation of the surface energy is primarily achieved through dimerisation of surface atoms to 'soak up' dangling bonds causing changes in the symmetry of the surface layers. Dimerisation is a common process for energy minimisation on (001) surfaces of diamond and zinc blende semiconductors. For GaAs(001) the dimerisation of surface atoms induces a well-defined two-fold periodicity in a direction parallel to the planes containing the dangling bonds with one dimensional disorder in the orthogonal direction (Dobson 1982).

The structure and stoichiometry at the surface of a III-V semiconductor material can critically depend on the growth conditions during epitaxy, for example the substrate temperature and the arrival rate of different atoms at the semiconductor surface, giving a variety of ordered surface reconstructions over a wide compositional range. MBE usually uses an excess of the group V element and typically the final layer of the MBE grown GaAs surface is As terminated. The wide variety of surface reconstructions associated with the GaAs(001) surface, ranging from the As-terminated c(4×4) surface through to the stable high temperature c(8×2) Ga-rich reconstruction, with decreasing As surface content and increasing temperature, are critically dependent on the exact surface stoichiometry. Under standard epitaxial growth conditions the GaAs(001)c(8×2) and (2×4) surface reconstructions are usually obtained. Fundamental interest in GaAs(001) arises as a consequence of the rich variety of surface reconstructions which can be formed by careful control of the epitaxial growth conditions.
The clean GaAs(001) surface has been the subject of many structural studies using many techniques including SXRD (Sauvage-Simkin et al 1989a, b), low energy electron diffraction intensity-voltage (LEED I-V) measurements (Mendez et al 1991), reflection high energy electron diffraction (RHEED) (Cho 1976, Larsen et al 1981, Dobson et al 1982) and scanning tunnelling microscopy (STM) (Biegelsen et al 1990, Gallagher et al 1992, Pashley et al 1988). Each reconstruction was generally made up of several As or Ga dimers in a particular arrangement and it was common to find several structures with the same symmetry present on the surface at one time. The stoichiometry varied over the surface. It was suggested that the GaAs(001)4x1 reconstruction was, in fact, an incompletely ordered c(8x2) Ga-terminated structure (Biegelsen et al 1990).

The strong interest in the GaAs(001) surface has not been restricted to the field of experimental physics and many theoretical investigations, including total energy calculations, have been performed to determine the nature of the reconstructed surface, the band structure and electronic properties of the surface (see, for example, Chadi 1987).

7.2.2 The Growth of Metals on III-V Semiconductor Surfaces

Many 3d metals have lattice parameters that closely match that of GaAs (5.654 Å) divided by two and therefore present themselves as ideal adsorbates for epitaxial growth on this substrate allowing the stabilisation of 3d metals in thin film form. The growth of 3d metals on compound semiconductor surfaces is generally complex, typically involving disruption of the semiconductor surface, resulting in atomic diffusion of the substrate species into and through the growing metal layer, producing non-abrupt interfaces, and occasionally accompanied by compound formation (see, for example, Cho 1976, Massies 1980, Neave and Joyce 1978, Bachrach 1979). The exact degree to which the above processes play a role in defining the interfacial structure and growth mode of the overlayer depend on the specific choice of adsorbate and substrate as well as the growth conditions. Common substrate and overlayer combinations were summarised in Table 2.1 (see Section 2.4). The termination of the semiconductor surface, either by Ga or As atoms, can influence the overlayer formation, for example, altering the Schottky barrier height for metal growth on differently terminated GaAs surfaces (Cho & Dernier 1978). Most experimental studies were performed on commercial GaAs wafer with no epilayer grown.

The magnetic and electrical properties of thin metal films depend critically on the film thickness, film quality and growth conditions. Ideally, for device applications one desires an abrupt, intimate contact between the metal and the semiconductor.
surface, without atomic intermixing or the formation of intermetallic compounds and a careful choice of the metal-semiconductor combination is needed to ensure optimum metal layer formation.

Many technological advances have been made through the incorporation of metal layers in heterostructures for device applications and sensor applications (Palmstrom and Morgan 1985), and fabrication of ultra-small ferromagnetic volumes (De Boeck et al 1993) and sub-\$\mu\$ structures (Shearwood et al 1994).

Co is hcp to 698 K, above which it is fcc until its melting point at 1765 K. The bcc Co phase does not naturally appear on the thermodynamic phase diagram, but was predicted from a study of the lattice parameter of the Fe\_xCo\_(1-x) alloy as a function of percentage composition (see Section 2.5.1, Figure 2.3). The predicted lattice constant for the bcc Co phase was 2.819 Å (Ellis and Greiner 1941), which has a lattice mismatch of 0.2 % with GaAs (divided by two) making GaAs an ideal substrate on which to stabilise the predicted bcc phase of Co by epitaxial growth (Bland 1991a, b, Xu 1987).

The bcc Co phase was first stabilised by MBE on the (110) face of GaAs by Prinz et al (1985) and the lattice constant was experimentally determined to be 2.82±0.01 Å. Bcc Co overlayer growth on the GaAs(110) surface showed only slight disruption of the semiconductor surface (Xu et al 1987). Growth on the (001) face of GaAs, however, was more complicated. Prinz (1991) reported that growth proceeded through the formation of epitaxial islands in registry with the substrate with eventual coalescence into a continuous film. The crystalline quality of the film was found to be lower than that on the GaAs(110) surface, with only partial order of the Co overlayer being induced by the substrate. Considerable substrate disruption of the GaAs(001)c(8\times2) surface was observed by Xu et al (1987) causing Ga and As intermixing with the growing metal overlayer inducing only a weakly ordered epitaxial film of bcc Co. An undistorted bcc structure was reported to exist by the fourth monolayer of Co (Jonker et al 1991). Figure 7.1 shows the epitaxial orientation of bcc Co on GaAs(001).

Bcc Fe (a\_0=2.866 Å) films grow with a low energy, close packed surface providing a good opportunity for fabricating an abrupt, flat metal-semiconductor interface by MBE, enabling the coupling of semiconductor logic and non-volatile magnetic memory. A study by Waldroup et al (1979) using XPS and LEED showed that Fe grew epitaxially on GaAs(001) forming a non-abrupt, chemically reacted region several Å thick at the overlayer-substrate interface. Again, Ga and As dissociated at the interface accompanied by As surface segregation. The growth was in a predominantly layer-by-layer mode with the first Fe layer bonded strongly to the substrate (Waldrup and Grant 1979). Fe films fabricated on GaAs(001), using metal
Figure 7.1 The orientation of the bcc Co phase when epitaxially grown on the GaAs(001) surface. Vectors $a_1$, $a_2$, and $a_3$ define the surface notation used.
organo chemical vapour deposition (MOCVD) by decomposition of Fe(CO)$_5$ at heated substrates, possessed a high degree of crystallinity (Kaplan et al 1983).

7.3 Experimental Details

The experimental equipment has previously been described in detail in Chapter 4. Co (of purity 99.999%) and Fe (99.9998%) were evaporated from Knudsen cell sources. The GaAs(001) substrate preparation need only be described here. The full procedure for preparation of semiconductor substrates for SXRD experiments is given in Appendix A. The coverage of the deposited films was independently determined by RBS analysis (Jeynes et al 1995).

7.3.1 $\alpha$-As Capped GaAs(001) Substrates

The experimental substrates were fabricated by MBE onto commercially available (001) oriented GaAs wafer (Johnson 1994). The wafer was first cleaned in solvent, etched, rinsed and dried before introduction into the MBE chamber, where the surface was Ar ion bombarded and annealed until a c(2×8) reconstruction was observed by RHEED. A 3000 Å thick GaAs(001) epilayer was grown on the clean GaAs(001)c2×8 surface and immediately capped with a thin amorphous As layer to passivate the freshly grown epilayer and to protect the MBE surface when the substrate was removed from the MBE chamber.

The $\alpha$-As capped GaAs(001) wafer was then cleaved into 8×8 mm$^2$ pieces and indium bonded to a Mo backing plate for surface x-ray diffraction experiments, as illustrated in Figure 7.2 (see Appendix A).

7.4 Results

Reported here is a study of the capped GaAs(001) surface, the decapping procedure and the subsequent structure of the restored surface, followed by investigation into the growth mode and overlayer structure of Co and Fe films prepared by MBE on the decapped GaAs(001)$_4$×1 surface. The techniques used were SXRD, AES, SEM and RBS.

7.4.1 $\alpha$-As Capped GaAs(001) Substrates

In Plate 7.1 SEM images show the condition of the $\alpha$-As capped GaAs(001) surface after storage in air for several months. The condition of the capped surface used in
GaAs(001) Wafer

8 mm

8 mm

0.5 mm

10 mm

1 mm

Molybdenum Block

Thin In Layer

[001]

Figure 7.2 Schematic diagram of the In-bonded GaAs sample used for SXRD experiments.
Plate 7.1 SEM of the surface of the α-As capped GaAs(001) substrates after several months storage in air showing the formation of As$_2$O$_3$ crystallites (SEM performed by G.M.L. McTurt, University of Leicester 1995).
this work was similar to that observed by Resch et al (1992). Resch and co-workers performed a study of the stability of the \( \alpha \)-As capped GaAs(001) surface concluding that prolonged exposure to the atmosphere produced a highly inhomogeneous cap morphology with a random distribution of \( \text{As}_2\text{O}_3 \) crystallites, of 5-10 \( \mu \text{m} \) in size, atop of the \( \alpha \)-As cap.

To restore a clean, well-ordered GaAs(001) surface the protective \( \alpha \)-As layer was removed by sublimation under UHV conditions. The desorption process was monitored \textit{in-situ} by recording the variation of the x-ray specular intensity as a function of time. Desorption of the \( \alpha \)-As cap at 673 K was monitored at (0, 0, 1.09) position in reciprocal space, near the \textit{anti-Bragg} position of the GaAs(001) lattice. Figure 7.3 shows the measured variation in intensity during thermal desorption of the \( \alpha \)-As cap. A model to describe the stages of thermal desorption is shown in Figure 7.4(a)-(d) (after Resch \textit{et al} 1992). The first stage involves desorption of the \( \text{As}_2\text{O}_3 \) crystallites from the inhomogeneous surface of the \( \alpha \)-As cap at a temperature of 433 K, accompanied by partial removal of the \( \alpha \)-As layer leading to the formation of \( \alpha \)-As islands. Following this, desorption of the main part of the cap occurred at about 623 K exposing the clean GaAs(001) surface. The four stages of desorption proposed by Resch \textit{et al} (1992) are identified on the measured data (in Figure 7.3 by (a)-(d)).

Figure 7.3(a) shows a drop in the specular intensity when the desorption process started due to a roughening of the GaAs(001) surface. The \( \text{As}_2\text{O}_3 \) crystallites desorbed from the cap at this stage. Desorption of the main part of the cap coincided with the minimum reached in the curve, (b) in Figure 7.3, and a pressure burst in the UHV chamber. As the clean surface was restored the specular intensity increased and at the end of desorption was larger than that prior to heating, indicating a smoother surface as would be expected for the MBE grown GaAs epilayer.

The clean GaAs(001) surface reconstruction observed after decapping had a 4x1 periodicity, determined from the positions of fractional order reflections along the principal axes. Figure 7.5 shows a 4x1 fractional order peak from the reconstructed GaAs(001) surface. Given that the full-width-at-half-maximum (FWHM) of the peak was 0.25°, the domain size of the surface reconstruction was determined to be about 1160 Å.

Auger electron spectroscopy (AES) measurements showed strong Ga and As peaks, a residual amount of carbon, but no oxygen.
Figure 7.3  Monitoring the specular reflectivity (0, 0, 1.09) during thermal desorption of the α-As cap. Heating was started at t=3 minutes (~673 K), and finished at t=30 minutes.
Figure 7.4 Four step desorption model (after Resch et al 1992) (a) initial intensity of the α-As capped surface after storage in air (prior to heating), (b) desorption of As$_2$O$_3$ crystallites, and partial removal of the α-As layer leading to island formation, (c) α-As still present on the surface at the original crystallite sites, (d) As completely removed to expose GaAs(001) surface.
In the literature substrates were prepared by varied methods, including sputtering and annealing cycles, α-As capping and in-situ growth of epilayers. The nature of final surface will vary with the preparation method and may affect subsequent growth. Gallagher et al (1992) suggested that the substrate decapping procedure did not compromise the quality of the GaAs(001)2×4 surface, although As from the cap was observed to adhere to step edges on the substrate. On the other hand, Biegelsen et al (1990) reported that the surface order was much better for the samples prepared in-situ than those treated with the As-capping technique during a study of the GaAs(001)c(2×8) surface. The surface quality of decapped samples will nevertheless be higher than those prepared by sputtering and annealing cycles since substrate damage is inherent in ion bombardment.

7.4.2 The Clean GaAs(001) Surface Structure

A brief analysis of the clean GaAs(001)4×1 surface is first presented. The decapped GaAs(001) surface showed a 4×1 reconstruction, also observed by Resch et al (1992) who treated GaAs samples in the same manner. A full structural analysis was not performed on the clean surface since the work here was concerned with metal growth on GaAs, however, important information about the surface termination and roughness can be gained from specular rod scans, which can be measured in a relatively short time. Such information is useful when determining the interaction of the deposited metal film with the substrate. In the analysis of the adsorbate covered surfaces the reconstruction was assumed to be destroyed on metal deposition (supported by RBS analysis which showed disruption of the substrate upon Co deposition).

The measured specular rod data for the clean GaAs(001)4×1 surface was analysed using different surface models which varied by atomic termination and dimer configuration in a 4×1 unit cell. A c(8×2) Ga-terminated surface model was also compared with the measured data, after Biegelsen et al (1990), who suggested that GaAs(001)4×1 surface was, in fact, a partially ordered c(8×2)-Ga structure.

Figure 7.6 shows the measured specular rod for the clean GaAs(001) surface with the best fit results. The best fit to the data for the models tested was obtained using a (4×1) As-terminated surface which was not fully reconstructed (about 20% of the surface was unreconstructed), with a best fit χ² of 1.38. The rms roughness model could not be fitted to the measured data suggesting that the roughness was of another form. There was a large outward displacement of the dimer units above the GaAs(001) surface (about 1.15 Å).
Figure 7.5  
4×1 fractional order peak (0.5, 0, 0.05) from the reconstructed GaAs(001) surface after thermal desorption of the cap (FWHM = 0.25°), from which the domain size of the reconstruction was determined to be about 1160 Å.
Figure 7.6 Measured specular rod for decapped GaAs(001)4×1 surface showing the fit to the model described in the text.
In conclusion, the clean decapped GaAs(001) surface is As terminated with a (4x1) periodicity. The atomic termination of the surface is the important result here since the metal overlayer interaction will ultimately begin with at topmost layer.

7.4.3 The Growth of Co on GaAs(001) at 300 K

The Growth Mode of Co on GaAs(001)

For a full picture of the overlayer growth mode it is important to monitor the x-ray intensity variation at different positions in reciprocal space during deposition. Growth was performed at 300 K. Unfortunately, the anti-Bragg position for bcc Co is very nearly coincident with a Bragg peak originating from the bulk GaAs(001) at \( \ell=2 \) on the specular rod \( a_0(\text{GaAs})=5.654 \text{ Å} \) and \( a_0(\text{bcc Co})=2.82 \text{ Å} \), and therefore it was not possible to monitor the overlayer growth at the position most sensitive to the formation of monolayer height islands. The intensity during overlayer growth was monitored as close to this position as possible \( (\ell=1.93) \) trying to avoid saturation of the signal by the Bragg peak, with some success. Monitoring growth near the anti-Bragg position of the GaAs(001) lattice \( (\ell=1.09) \) did, however, provide sensitivity to overlayer growth. The Co deposition rate was 1 monolayer in 10 minutes.

Figure 7.7 shows the measured variation in specular intensity as a function of deposition time for the growth of Co on GaAs(001) at a substrate temperature of 300 K at (a) \( \ell=1.93 \), and (b) 1.09 Rlu. RBS and AES measurements confirmed intermixing of As and Ga within the overlayer. RBS analysis showed disruption of the substrate upon Co deposition. Metal deposition caused liberation of Ga and As from the substrate. The liberated Ga atoms have sufficient mobility to form Ga islands on the surface and Ga droplets were observed in SEM measurements. It was possible that the Ga detected in AES and RBS was in this form.

In Figure 7.7(a) the growth curve measured at \((0, 0, 1.93)\) shows an initial fall, reaching a minimum at about 3 ML, due to roughening of the surface over several layers, presumably from out-diffusion of As and Ga atoms at the interface mixing with the Co overlayer. The growth is in a 3D manner. The growth then becomes better ordered, indicated by a gradual increase in the specular intensity which reaches a broad maximum at 8.5 ML. This results from coalescence of epitaxial 3D islands which developed during the initial stages of growth producing largely completed adlayers. The overlayer growth is predominantly in a 3D manner with no monolayer period oscillations observed.
Figure 7.7  The measured variation in specular intensity as a function of deposition time for the growth of Co on GaAs(001) at a substrate temperature of 300 K at (a) $t=1.93$, and (b) 1.09 rlu.
Figure 7.8  (a) side view of model of calculated Co overlayer structure, (b) simulated growth curves at $I=1.09, 1.36, \text{and } 1.93$ rlu.
The curve measured at (0, 0, 1.09) during the growth of Co on GaAs(001) (Figure 7.7(b)) showed an initial drop and a weak oscillation, after which the curve is featureless. This again supports a 3D growth mode.

Figure 7.8 shows the calculated intensity variation expected for ideal (single) layer-by-layer growth of Co layers on GaAs(001) at perpendicular momentum transfer values of $\xi=1.93$ and 1.09 rlu for the model illustrated. The calculated curves in Figure 7.8 do not take account of any intermixing with substrate species at the interface. Both the calculated curves show an initial fall in intensity to a Co coverage of about 0.5 ML, followed by a rise which reaches a maximum at 1 ML, after which the behaviour is dependent on the point in reciprocal space at which the observation is made. Co overlayer growth at (0, 0, 1.93) was characterised by shallow cusps of monolayer period. Growth at $\xi=1.09$ rlu showed parabolic curves with a monolayer period.

For the above calculation the model shown in Figure 7.8 was used. The d-spacing of the overlayer was calculated using simple geometrical relationships given below. The (tetrahedral) covalent radii of Ga and As are 1.26 Å and 1.18 Å respectively and the (12 co-ordinated metallic) radii of Co and Fe are 1.25 Å and 1.26 Å respectively (American Institute of Physics Handbook 1963). A uniformly flat Co overlayer covalently bonded to the bulk terminated substrate surface with an abrupt, non-intermixed interface was assumed. Based on these data the height of the Co monolayer above the bulk terminated GaAs(001) surface and the d-spacing of the bcc Co epitaxial film were 1.47 Å (within a hard-sphere model) and 1.40 Å (using a value for Poisson’s ratio of 0.35, typical of a bulk metal) respectively. When the bcc phase of Co is stabilised on the bulk terminated GaAs(001) surface a lattice expansion of the overlayer in the plane of the surface is induced by the GaAs unit cell, resulting in a contraction of the interlayer spacing perpendicular to the substrate surface. Poisson’s ratio is given by the contractile strain divided by the linear strain for the lattice and the d-spacing of the epitaxial film can be calculated taking overlayer expansion or contraction into account.

The measured growth curves (Figure 7.7) do not display the behaviour shown in Figure 7.8. The calculations confirm that overlayer growth did not develop in a layer-by-layer mode (Frank van der Merwe mode) for which monolayer period intensity oscillations would be expected. The form of the experimentally measured growth curves was more consistent with the formation of 3D epitaxial islands which merged into a continuous film at higher coverage.
Figure 7.9 Summary of specular rod data recorded at Co coverages of (a) 1.1 ML, and (b) 2.23 ML showing fits to the models described in the text.
Figure 7.9 summary of specular rod data recorded at Co coverages of (c) 8.83 ML and (d) 15.83 ML showing fits to the models described in the text.
The Evolution of the Co Overlayer

By following the variation in specular intensity during deposition it was concluded that the Co overlayer evolved in a 3D manner. Using this approach, information is only derived from a single point in reciprocal space. A more quantitative method is to measure the x-ray intensity perpendicular to surface at specific overlayer coverages to provide information about the vertical film morphology. Specular rod scans were recorded at specific overlayer coverages.

Overlayer growth was interrupted at coverages of 1.1, 2.2, 8.8 and 15.8 ML and specular rod scans recorded at each coverage. Figure 7.9(a)-(d) summarises the specular reflectivity data, plotted as structure factor against perpendicular momentum transfer, along with fits to the models described in the text below. Each specular rod scan measures the variation in intensity as a function of \( I \) over the range from 0.11 to 3.04 rlu at each coverage. The observed fringes are a consequence of interference from a number of flat bcc Co layers, \( N \), of equal thickness, \( d \).

In Figure 7.9(a) the measured specular rod at a Co coverage of 1.1 ML is shown with fits to models described below. A bulk terminated GaAs(001) substrate with no reconstruction was considered. The dotted line is the scattering from the bulk GaAs(001) lattice, the dashed line is a fit with a flat overlayer of Co, and the solid line is a best fit to a three-layer overlayer model.

Fitting a flat adlayer of Co to the measured specular reflectivity data produces a very poor fit, apparent by visual inspection (giving a reduced \( \chi^2 \) of 4.70). The rms roughness was high for a semiconductor surface at 3.9 Å. It can be immediately concluded that the Co adatoms do not initially coalesce into flat adlayers on the GaAs(001) surface.

A much better fit to the data was obtained when a three-layer model was compared with the measured data, giving a \( \chi^2 \) of 2.26. Physically, this implies that the Co overlayer evolved in a 3D manner in the initial stages of growth confirming the earlier conclusions made from the real time growth curve. In the three-layer model the occupancy and displacement of the layers was freed-up in the analysis. The overall overlayer thickness was contracted by 5.7%, with each d-spacing, from the metal-semiconductor interface upwards, individually contracted by 0.91%, 2.80% and 1.97% respectively. The occupancy of the layers varied as 82.0%, 76.6%, and 30.9% respectively. This gives a total film coverage of 1.9 ML, whereas only 1.1 ML of Co was deposited. The high coverage was interpreted as intermixing of As and Ga with the metal overlayer. The proposed overlayer structure is shown in Figure 7.10.
Figure 7.10 Proposed overlayer structure for Co/GaAs(001) at a coverage of 1.1 ML. A three-layer model describes the overlayer morphology. Excess coverage is attributed to intermixed substrate atoms.
Incidentally, the rms value of 3.9 Å obtained by fitting a flat Co adlayer is equivalent to a Co film height of 2.8 ML which seems to verify the conclusion that the overlayer is made up of the three layers. Essentially this layer structure is a model of surface roughness. The form of the roughness, however, is different from the beta roughness model, in which the occupancy of consecutive layers is given by $\beta$, $\beta^2$, $\beta^3$, etc. ($0<\beta<1$). In the proposed model the first two layers were equally occupied (approximately) with a 30% occupancy in the top layer.

Figure 7.9(b) shows the measured specular reflectivity at a Co coverage of 2.23 ML. Interference fringes in the curve which could be fitted using a model consisting of five bcc Co layers with a $\chi^2$ of 4.46 and $\sigma_{\text{rms}}$ of 4.7 Å. Therefore, at a coverage of 2.23 ML the growth mode is still predominantly in a 3D manner and can be characterised by the simultaneous occupancy of several layers. The film is very disordered. The layer occupancy and position were fixed in this case. If the parameters were freed-up then unphysical values were obtained for the occupancy and displacement parameters. In this case the total coverage was 5 ML, the excess material again attributed to As and Ga intermixing. There was a large discrepancy in coverage by this stage.

Figure 7.9(c) shows a fit to the specular rod at a coverage of 8.83 ML with a poor $\chi^2$ of 7.1. The surface model consists of 10 ML of bcc Co. By this coverage a well established bcc Co film existed (Jonker et al 1991) and therefore a model simply consisting of bcc Co layers was fitted. This coverage corresponds to the maximum intensity observed in the original growth at $l=1.93$. The overlayer predominantly consisted of bcc Co layers at this stage.

At a coverage of 15.8 ML (Figure 7.9(d)) the interference fringes in the data could be fitted with a model consisting of 16 ML of bcc Co. The fit to the fringes gets progressively worse with increasing $l$ indicating a rough metal-semiconductor interface. The $\chi^2$ was 5.35 and the rms roughness 1.32 Å.

In summary, the morphology of the Co film in the low coverage regime was characterised by simultaneous occupancy of several layers resulting in a 3D film evolution. The As and Ga substrate atoms released upon metal deposition became incorporated in the metal overlayer. The fitting indicates an artificially high coverage of material at the surface at low coverage. As the film developed the bcc layer structure improved.
Intermixing at the Co-GaAs(001) Interface

In the above analysis the effects of As and Ga intermixing at the metal-semiconductor interface were not taken into account, although shown to occur.

Analysis of the interference fringes observed from a thick overlayer (26 ML) provided information about the interlayer spacing, the number of layers, and the composition of the film. A thick film was used to characterise the interfacial intermixing for two reasons. Firstly, at a higher coverage the overlayer structure is well defined, i.e. a bcc Co lattice. Secondly, the intermixing can extend a considerable distance from the interface, up to 20 Å, and a film of sufficient thickness is required to include this length range.

A thick film of Co was deposited onto the clean GaAs(001)4×1 surface in a single deposition at a substrate temperature of 300 K whilst monitoring the real time variation in specular intensity at (0, 0, 1.93) (already shown in Figure 7.7(a)).

The specular rod scan recorded at a coverage of 26 ML showed interference fringes corresponding to 26 ML of bcc Co, similar to Figure 7.11. The fringes were well defined at small perpendicular momentum transfer values and a model of the intermixing was tested in this region. A simple model of the interfacial interdiffusion was fitted to the measured data, based on an exponential function decay of As from the interface. Only a restricted number of exponential functions were tested since a comprehensive analysis of the intermixing was not possible using the present software. The sensitivity of XRD to the intermixed region is expected to be limited since the atomic numbers of the elements are similar.

The measured data were consistent with 26 ML of bcc Co in agreement with the RBS analysis. The morphology of the overlayer was disordered, with an rms roughness (σrms) of 9 Å at the film surface. The roughness was a combination of 3D layer growth and substrate out-diffusion. An exponential decay of As from the metal-semiconductor interface was included in the model and fitted to the data. Arsenic atoms were substitutionally placed into the Co matrix and the profile of the As decay was described by the following equation for 26 ML of Co on GaAs(001) (Eq. 7.1):

\[ C_{\text{As}}(\text{Co}) = a \exp(-bx) \]  

(7.1)

where \( C_{\text{As}}(\text{Co}) \) is the fraction of As incorporated in the Co layer at a distance \( x \) (in monolayers) from the metal-semiconductor interface. The constants \( a \) and \( b \) were determined to be 0.75±0.25 and 0.33±0.1 ML\(^{-1}\) from the analysis.
Figure 7.11  Structure factor vs. perpendicular momentum transfer for specular reflectivity at 26 ML of Co/GaAs(001) deposited at 300 K, showing the best fit to the data for a model including an exponential decay of As from the interface (described in the text).
Surface Segregated As and Ga Atoms

Intermixed Overlayer Region

Original GaAs Bulk Level

Heavily Intermixed Co, Ga and As

Figure 7.12 Schematic of surface structure and composition of Co/GaAs(001) film.
There was a considerable amount of As present at the interface during the initial stages of film formation, up to a concentration as high as 75%, decaying exponentially from the interface, according to Eq. (7.1). The concentration of As was found to be insignificant 7 ML (~10 Å) from the interface, with a best fit $\chi^2$ of 0.95 (Figure 7.11). The $\chi^2$ values did not differ significantly between the different models tested. Ga intermixing will also be present at the interface, but the computer modelling was restricted to a limited number of parameters, and these data were best represented with As atoms incorporated in the lattice. In fact, the exponential profile in Eq. (7.1) effectively included As and Ga atoms, however, As is the dominant impurity. The SXRD measurements were not particularly sensitive to the exact nature of the intermixing, however, by separately substituting Co and Ga for As in the above model we derive important information about the chemical composition of the overlayer. When Co or Ga atoms replace the As atoms in the model proposed above the best fit $\chi^2$ values are significantly worse (1.34 and 1.44 respectively) confirming that As is the main contaminant of the Co film. The former case is equivalent to pure elemental Co overlayers and, since this does not describe the measured data as well, reinforces the existence of intermixing at the interface. Figure 7.12 shows a schematic diagram of the proposed structure of Co covered surface at 26 ML.

The sensitivity of SXRD to the film components is limited but nonetheless it is possible to determine certain aspects of the chemical composition.

### 7.4.4 The Effects of Annealing the Co Film at 773 K

A 50 ML thick film of Co grown on GaAs(001) at 300 K was annealed at 773 K for 7.5 minutes. An initial anneal at a lower temperature of 563 K produced no detectable structural change in the film. After annealing a peak appeared in the specular rod at $\ell=2.71$ rlu. The diffraction peak corresponded to the spacing between the basal planes of the hcp structure ($c/2=2.04$ Å). The anneal provided sufficient energy to allow the bcc Co structure to relax to its bulk phase and Co islands were formed. The disappearance of interference fringes present for the as-grown film indicated that the film became highly disordered upon annealing.

RBS analysis of the annealed film showed reduced amounts of Ga and As in the surface, perhaps as a result of desorption during the anneal. Annealing caused Co to diffuse into the substrate. Once again, the Co film induced substrate damage.
7.4.6 The Growth of Fe on GaAs(001) at 300 K

Presented here is a comparative study of the growth of Fe on the GaAs(001) surface. Fe was deposited on the clean GaAs(001)4\times1 reconstructed surface at 300 K at a chamber pressure of 5\times10^{-10} mbar. The total Fe coverage was determined by RBS analysis and the deposition rate was one monolayer of Fe in 12 minutes.

The Growth Mode of Fe on GaAs(001)

Figure 7.13 illustrates the variation in specular intensity for the growth of Fe on the GaAs(001)4\times1 surface, measured at (a) \(\theta=1.09\) and (b) 1.78 rlu. The growth of Co on GaAs(001) in Figure 7.7(b) can be directly compared to Figure 7.13(a), as both were measured at (0, 0, 1.09) and also the deposition rates for Fe and Co growth are similar.

In Figure 7.13 (b), after an initial intensity fall, we observe weak, damped intensity oscillations indicating a propensity towards layer formation in the early stages of growth, albeit poor quality. The period of the oscillations were irregular and not of a monolayer period. The first oscillation had a period of 23 minutes, whereas the latter two were about 30 minutes and of weaker intensity, suggesting that a multilayer growth mode was occurring.

The oscillations are stronger than in the equivalent measurements for Co growth on the same surface, suggesting that Fe has a greater tendency for two-dimensional growth on GaAs(001) producing better ordered, higher quality films.

Intermixing at the Fe-GaAs(001) Interface

The intermixing profile was determined from a thick Fe overlayer. Fe was deposited on the clean GaAs(001)4\times1 surface at 300 K in a single deposition up to a coverage of 29.4\pm1.5 ML, determined by RBS analysis. The experimentally measured growth curve, recorded at (0, 0, 1.78), during deposition was previously shown in Figure 7.13 (b). An initial intensity drop is followed by a single weak oscillation, of a 30 minute period, after which the growth curve is featureless. Following a similar analysis to that previously described for the Co covered surface the diffusion gradient of As in the Fe film can be described by:

\[
C_{\text{Fe}} = a \exp(-bx)
\]

where \(C_{\text{Fe}}\) is the fraction of As incorporated in an Fe layer at a distance \(x\) (in monolayers) from the metal-semiconductor interface, and the constants \(a\) and \(b\) are...
Fe/GaAs(001) growth curves (a) 1.09 (9.1 ML), and (b) 1.78 rlu (29.4 ML) respectively.
given by 0.25±0.25 and 0.33±0.8 respectively on this occasion. The As decay from the metal-semiconductor interface in the Fe overlayer follows the same decay profile as that for Co films on GaAs(001), but with a significantly lower concentration of As at the metal-semiconductor interface, reduced to 25% in the first Fe monolayer (giving a χ² of 0.65).

Fe is a more reactive element than Co and, in consequence, the adsorbed Fe layer is more strongly bonded at the substrate surface producing a metal film with higher metal content. Subsequent metal-on-metal layer growth is better ordered.

RBS analysis showed that the Fe film had induced substrate damage and the presence of As and Ga in the surface of the film was detected.

7.5 Conclusions

The interaction of transition metals with the GaAs(001) surface was considerably more complex than that in metal-Si(001) systems (see Chapter 8). Ga and As are almost isoelectronic, with atomic numbers of 31 and 33 amu respectively, making it difficult, although not impossible, to distinguish the individual scattering contributions using x-ray diffraction. It was possible to identify the elemental composition of the overlayer to a certain extent, for example, identifying that the film was not composed purely of Co atoms but contained As as the main impurity. Element specific probes was used in conjunction with x-ray measurements.

The bcc phase of Co developed in a predominantly 3D growth mode on the GaAs(001) surface, as epitaxial islands which eventually formed completed layers at a coverage of about 8.5 ML. The deposited Co film induced substrate damage and promoted out-diffusion of As and Ga atoms to the surface of the growing layer. Analysis of the Co film showed a structure consistent with the bcc Co phase with a d-spacing of 1.40 Å, with the first Co layer at a height of 1.47 Å above the GaAs surface. Annealing the as-deposited film resulted in diffusion of Co into the substrate and development of hcp Co islands.

The growth of Fe on GaAs(001) showed better-ordered overlayer growth with a greater tendency towards a 2D growth mode. Once again the Fe film induced substrate disruption, promoting the release of substrate species, but to a lesser extent, with reduced incorporation of substrate atoms in the metal film. The film structure consisted of Fe layers with an d-spacing of 1.46 Å supported 1.54 Å above the substrate.
Chapter 8
The Growth and Atomic Structure of Metal Adsorbates on the Si(001) Surface

8.1 Summary

The growth mode, atomic structure and substrate interaction of In and Ga overlayers, produced by MBE, on Si(001) have been studied as a function of adsorbate coverage and substrate temperature. We interpret data from a number of analytical techniques including SXRD, LEED and AES.

The formation of In overlayers on the Si(001)2×1 surface followed a Stranski-Krastanov growth mode at all substrate temperatures between 300 to 623 K, i.e. the formation of a single monolayer of metal after which three-dimensional (3D) islands coalesced. At room temperature Ga nucleated in a 3D manner on Si(001), whereas improved growth was observed at higher temperature.

Varied overlayer reconstructions were observed by LEED as a function of temperature and coverage. From 300 to 373 K a Si(001)2×1-In surface reconstruction existed from a coverage of 1 monolayer (ML). The Si(001)2×2-In reconstruction was observed by LEED at a coverage of 0.5 ML for substrate temperature below 423 K. The Si(001)3×4-In reconstruction appeared at a higher substrate temperature for the same coverage. The interaction of the adsorbed metal atoms with the substrate reconstruction was determined from changes in the fractional order diffraction peaks, which originate from the Si(001)2×1 surface reconstruction, as a function of metal coverage. In caused only minimal substrate disruption at 300 K, whereas both metals strongly interacted with the underlying dimerised Si surface at 373 K. The Si(001)2×1-In reconstruction was formed at a coverage of 1 ML by the substitution of In dimers for Si dimers determined by SXRD. The Si(001)2×2-In reconstruction could not be observed using x-ray diffraction, presumably because the correlation length of the reconstruction was too small to measure.

It was found that contamination of the Si(001) surface by carbon influenced the epitaxial growth producing disordered overlayer formation.
8.2 Metal-Silicon Interfaces and Surface Reconstructions

Although the Si(lll) surface has been extensively studied in the past (see, for example, Landers & Morrison 1965, Baba et al 1980, 1982, Nguyen et al 1974a, b) relatively little work has been reported for the technologically more interesting (001) face of Si. This is partly due to the experimental difficulties associated with preparing clean, high quality Si(001) surfaces. The behaviour of a given metal on these two surfaces can be quite different, particularly at low metal coverages and low growth temperatures, where the metal is most strongly influenced by the clean surface reconstruction. For example, at a substrate temperature less than 423 K In adatoms have sufficient mobility on Si(001) to form stable structures without significant alteration of the underlying surface reconstruction, contrasting the growth of metal overlayers on the Si(lll) surface (Landers and Morrison 1964a, b, Zegenhagen 1989).

Upon truncation of the bulk Si(O01) lattice, a new periodic surface structure is formed which achieves a minimum free energy through rearrangement and relaxation of the atom positions in first few surface layers. In the case of Si(001) the topmost Si atoms dimerise giving a 2x1 periodic structure. The Si(001)2x1 surface reconstruction is highly furrowed with rows of Si dimers extending along the <110> axes and, in consequence, the reconstruction strongly influences the growth of metal adlayers at sub-monolayer coverages. The reconstruction induces highly asymmetric adsorbate overlayer growth. Although low energy electron diffraction (LEED) (Knall et al 1986) and scanning tunnelling microscopy (STM) studies (Baski et al 1991) have provided much information about the growth of metal overlayers on Si, the local atomic structure has not been fully established and an understanding of the early stages of film growth on the Si(001)2x1 surface is required.

Figure 8.1 shows the surface phase diagram for In on Si(O01) (after Knall et al 1986). Many different metal induced phases exist as a function of In coverage and substrate temperature, as discussed below. An additional phase not present on the phase diagram may be formed by annealing the 2x1-In structure, formed at a coverage from 1 to 3 ML and a temperature of 273 to 423 K, to about 573 K where a 1x1 reconstruction is induced (Kuwata et al 1984).

The growth of In on the Si(001) surface proceeds through various coverage and temperature dependent stages. Initially, a 2D metal gas forms on the Si surface (below a coverage of ~0.1 ML), but, with increasing metal coverage, the evolution of ordered surface reconstructions was observed using electron diffraction techniques (Knall et al 1986). All overlayer coverages are referenced to the
Figure 8.1 Surface phase diagram for In on Si(001)2×1 (after Knall et al 1986)
unreconstructed Si(001) surface, for which 1 monolayer (ML) is defined as 6.8x10^{14} \text{ atoms cm}^{-2}. For a temperature range between 300 and 423 K, rows of In ad-dimers were arranged on the Si(001) surface with varied inter-row spacing at low metal coverage (0.1 to 0.3 ML). Stable structures with (3\times2) and (5\times2) periodicity were observed at specific coverages in this growth regime. These low coverage phases are stabilised by the repulsive ad-dimer row-row interactions and the disruption of the top most surface Si layers by the adsorbed metal atoms may be related to the row-row interactions (Kuwata \textit{et al} 1984). Many of the metal films (for example In, Ga, and Al) grown on Si(001) behave in a similar manner (Ide \textit{et al} 1989).

With increasing metal coverage a Si(001)2\times2-In phase develops in coexistence with the 2\times1-Si substrate reconstruction. The In-induced 2\times2 reconstruction existed between 0.03 and 0.5 ML coverage (Baski \textit{et al} 1991). Minimal disruption of the underlying Si-Si dimer bonding occurred. The evolution of the phase was complete at a coverage of 0.5 ML, where total saturation of the Si(001) dangling bonds occurred. The 2\times2 phase has also been reported for Ga-covered Si(001) surfaces (Sakama \textit{et al} 1994).

Different models have been proposed for the metal induced 2\times2 reconstruction on the Si(001) surface which essentially differ on the orientation of the metal ad-dimer with respect to the underlying Si surface, i.e. whether the adatom dimer sits orthogonal or parallel to the underlying Si dimer structure, as shown in Figure 8.2. STM measurements were consistent with either model since the authors were unable to resolve individual atoms within the dimer structure (Baski \textit{et al} 1991). First principles energy calculations for Ga on Si(001), however, favoured the 2\times2 parallel ad-dimer model, shown in Figure 8.2(b), in which the Si-Ga bond lengths were in good agreement with the sum of the Pauling covalent radii leading to a structure with greater stability (Northrup \textit{et al} 1991). For coverages greater than 0.5 ML a transformation to the Si(001)2\times1 phase occurred at 1 ML coverage (Knall \textit{et al} 1986). The growth of 3D islands occurred at higher coverages.

For substrate temperatures above 423 K the deposited In adatoms formed a 4\times3 structure on the Si(001)2\times1 surface up to a coverage of 0.5 ML, at which point the 4\times3-In reconstruction was complete. Again, the growth of 3D islands predominated at higher coverages.

Technological interest in the Si(001) surface is wide reaching, including the heteroepitaxial matching of III-V compound semiconductors with Si, encouraged by the reasonable lattice match (~3.3%) and the desirable properties of Si as a
Figure 8.2  (a) Top view of the Si(001)2×2 orthogonal ad-dimer structure, (b) Si(001)2×2 parallel ad-dimer structure, after Northrup et al (1991), (c) side view of Si(001) with In dimer.
substrate. The bonding at the GaAs-Si(001) interface directly influences subsequent epitaxial growth and has, in consequence, been intensively studied (Bringans et al 1987, Smilgys et al 1990, Yoo et al 1993). Determination of the individual interactions of vapour deposited Ga (and As) adatoms with the reconstructed Si(001) surface will contribute to our understanding of the behaviour of deposited GaAs films. At present, little is known about the fundamental interactions of Ga (and As) with the Si surface. Furthermore, vapour deposited metal films form reduced dimensional structures at low metal coverage on Si(001) (Baski et al 1991, Knall et al 1986) which are of fundamental interest and technological profit. The deposited In atoms dimerise, to satisfy the dangling bonds of the Si(001)2×1 surface, giving rise to rows of metal ad-dimers which represent quasi one-dimensional chains, the study of which gives insight into the nature of low dimensional structures in general. Quasi one-dimensional chain structures may exhibit novel quantisation and structural behaviour not observed in higher dimensional arrangements.

8.3 Experimental Details

The UHV environmental chamber used to conduct the study has previously been described in detail in Chapter 4. For this work the chamber was equipped with Knudsen cell vapour sources loaded with 99.999% purity In and 99.995% purity Ga. 1 ML of In was deposited in 12 minutes (i.e. 0.0014 ML s⁻¹), and 1 ML of Ga in 15 minutes, determined from ex-situ Rutherford back scattering (RBS) analysis. The chamber pressure during deposition was ≤ 5×10⁻¹⁰ mbar.

The Si samples, 10×8×1 mm³ in size, were cut from commercial wafer and syton polished to within ±0.05° of the [001] crystallographic axis. A clean Si(001) surface was prepared using a wet chemical process prior to introduction into the UHV chamber (full instructions are given in Appendix A). Each sample was degreased in an ultrasonic bath of propanol (IPA), submerged into a hot H₂O:NH₄OH:H₂O₂ solution (5:1:1) to remove residual organic contamination, after which the Si surface was etched with a HF:H₂O solution (1:20), and finally re-oxidised by submersion into a hot H₂O:HCl:H₂O₂ solution (6:1:1). The wet chemical process removed any residual contamination, primarily carbon, from the Si surface leaving a clean, stoichiometric SiO₂ surface film at the end of the process (Yang et al 1985). After etching, the Si sample was mounted on the electron beam heater assembly and loaded into the UHV chamber. The thin oxide layer was removed in vacuo by annealing to 973 K for 10 minutes, and flashing to 1273 K for 2 minutes, followed by a slow cool down to 300 K, giving a sharp Si(001)2×1 LEED pattern (see Section 8.4.2, Plate 8.1(a)), with no indication of oxygen or carbon
contamination, within the detection limits of AES. An infra-red optical pyrometer was used to monitor the surface temperature during annealing. The chamber pressure remained in the 10^{-10} mbar range during the cleaning procedure.

From SXRD measurements it was found that the high temperature flashing (at 1273 K) was an essential step for obtaining high quality reconstructed Si(001) surfaces, determined from the full-width-at-half-maximum (FWHM) of the fractional order diffraction peaks of the Si(001)2×1 reconstruction, which give direct information about the quality of the surface reconstruction.

Re-use of Si(001) Samples

It was found possible to use the Si(001) samples for several metal depositions after treatment with an indium-beam-assisted (IBA) cleaning procedure to restore the original Si surface, as described below. The method was utilised during the In on Si(001) measurements. A similar procedure was reported by Yang et al. (1985).

After deposition of In, the overlayer film was first desorbed by annealing the sample to 1073 K for 2 minutes, after which the in vacuo cleaning procedure (described above) was repeated except with the In beam incident on the sample during the first anneal. The presence of the In adatoms on the hot Si surface benefited the cleaning process, aiding removal of any contaminants without causing craters or in-diffusion at the Si surface. The In beam was turned off during the flashing (1273 K) and cooling cycle to prevent indium being present on the surface at the start of deposition. The cleaning procedure was repeated until there was no oxygen or carbon contamination present on the Si surface and sharp, intense fractional order peaks were restored.

Metal growth onto the restored sample surface, monitored by AST and SXRD, was consistent with depositions on the original surface indicating that the original clean surface had been restored. The In-beam-assisted cleaning and deposition cycles could be repeated several times without measurable degradation of the sample surface. Eventually contamination persisted in spite of the above procedure and a fresh sample was prepared.

A different treatment was followed for Ga covered Si(001) surfaces. The Si(001)2×1 surface reconstruction was retrieved simply by following the standard in-vacuo cleaning procedure stated above, without using atom beam-assisted-cleaning. The use of an In beam to aid the surface cleaning was avoided to
prevent contamination of the growing Ga film by In, which may have remained on the cooler parts of the sample heater and migrated onto the sample surface during the experiment. Ga beam-assisted cleaning was not attempted.

8.4 Results and Discussion

Presented here are the results of In and Ga deposition on Si(001) as a function of metal coverage and substrate temperature. Detailed AES results for In on Si(001) are first presented (Section 8.4.1), followed by a LEED study of the structures induced on Si(001) by In (Section 8.4.2), and, finally, a SXRD study of the growth mode of In and Ga, with simultaneous AES measurements, a study of the metal interaction with substrate and an investigation of the Si(001)2×1-In and Si(001)2×2-In reconstructions (Section 8.4.3).

The ability of SXRD to probe beneath the topmost surface layers and examine the structure at the overlayer-substrate interface is essential for a non-destructive investigation of the interaction of adsorbate atoms with the substrate.

8.4.1 AES Studies

The Growth Mode of In on Si(001)

AST curves for the growth of In on Si(001) at different substrate temperatures between room temperature and 623 K are shown in Figure 8.3 (for the Si KLL (92 eV) emission line), measured using a special experimental set-up which allowed continuous monitoring of the Auger signal during metal vapour deposition.

All AST curves show 'breaks' separated by linear sections in the early stages of growth characteristic of monolayer formation (see Section 3.3). The overlayer formation followed a Stranski-Krastanov growth mode at all substrate temperatures with the first monolayer completed at 12 minutes deposition time, confirmed by RBS analysis to be a coverage of 1.01±0.04 ML. The position of the second 'break' was dependent on the growth conditions. At 300 and 373 K the behaviour was somewhat unusual after completion of the first monolayer and will be discussed later. At a temperature dependent coverage 3D island formation superseded the 2D growth mode, indicated by a levelling of the AST signal. The loss of In from the surface became apparent at 623 K by an increase in the Si AST signal with time. The effect was significant at a substrate temperature of 673 K (not shown). Indium either simply desorbed from the hot Si surface, or material from the deposited 2D adlayer coalesced into 3D islands depleting the underlying
Figure 8.3  Si KLL Auger intensity (92 eV) vs. In deposition time for the growth of In on Si(001) at the substrate temperatures stated in the figure (a)-(e). The In shutter was opened at time t=0 minutes and closed at a time indicated by an arrow in each case. The ratio of the time between the first and second 'break' in each curve is 1:4, 1:2, 1:2, 1:1, and 1:1 respectively.
In layer and exposing the Si substrate. The mechanism is dependent on the energetics of the system. At 473 and 623 K the completion of the second monolayer was arrested by the premature development of 3D islands. The greater In mobility at higher substrate temperatures induced the formation of 3D islands.

The sticking-coefficient is a measure of the likelihood of a vapour deposited adatom remaining on the Si surface after initial contact. The sticking-coefficient of In on the Si(001) surface was independent of the substrate temperature in the early stages of growth (up to 1 ML). The sticking coefficient was assumed to be equal to unity. The temperature independence for the time of initial monolayer completion suggests that the In strongly bonds with the Si(001)2x1 surface up to a coverage of 1 ML.

As the coverage increased a change in the nature of the bonding occurred as the influence of the dimerised Si surface reconstruction on overlayer growth was reduced. At a coverage of 0.5 ML the Si dangling bonds were saturated by adsorbate atoms. Above this coverage In-Si bonds were replaced by In-In bonds. Subsequent growth was highly strained and rapidly relaxed to a lower energy formation (3D islands), indicated by the rapid breakdown of monolayer formation above a coverage of 1 ML at higher temperatures.

A deviation from the expected Stranski-Krastanov behaviour was observed at substrate temperatures of 300 and 373 K (Figure 8.3(a)-(b)). The second AST ‘break’ is expected at a coverage of 2 ML (or below) but did not occur until much later. Growth at 300 K is quite extreme in this respect. The ratio of the time between the first and second ‘break’ for each curve in Figure 8.3(a)-(e) is 1: 4, 1: 2, 1: 2, 1: 1, and 1: 1 respectively. The phenomenon can not simply be explained by island formation, which would produce an exponential decay of the Auger signal, or a change in the sticking coefficient. A change in the growth mechanism has occurred but, as yet, the behaviour is unexplained.

In summary, the overlayer formation followed Stranski-Krastanov growth mode, however, a deviation from this was observed at lower temperatures studied. The first metal adlayer was strongly bonded to the Si surface, indicated by the temperature independence of the sticking coefficient up to a 1 ML coverage.
The Effects of Contamination on Metal Growth

A sample was prepared for RBS analysis up to a nominal coverage of 2.0 ML at 300 K. The AST curve measured during growth (not shown) had poorly defined breaks and did not fall to the expected level. The abnormal shape of AST curve suggested that overlayer growth was contaminated in some way and carbon contamination was confirmed by AES. RBS analysis indicated a 1.82±0.07 ML film of In deposited on the surface, however, the layer was non-uniform with the indium distributed over some depth in the silicon, unlike the deposition of uncontaminated In layers which formed a sharp interface with the substrate (also determined by RBS). We therefore conclude that surface contamination significantly alters the growth mode of In films on Si(001). Knall et al (1986) also showed that small amounts of C contamination altered the overlayer growth.

8.4.2 LEED Studies

In Overlayers on Si(001)

After thermal treatment under UHV conditions the clean Si(001) surface produced a sharp, two-domain (2x1) LEED pattern, reproduced in Plate 8.1(a) at 300 K (shown at an electron beam energy (E_e) of 70 eV). Evaporation of In onto the clean Si(001)2x1 surface at different substrate temperatures induced varied LEED reconstructions. After deposition up to an In coverage of approximately 1 ML, at substrate temperatures from 273 to 423 K, a two-domain (2x1) LEED pattern was observed (not shown), which was similar to the clean substrate pattern. The pattern had a higher background signal and the diffraction spots were slightly reduced in sharpness compared to the clean surface. The deposition of In to a coverage of 0.5 ML at a temperature up to 423 K induced the Si(001)2x2-In surface reconstruction shown in Plate 8.1(b), measured at 65 eV, in which the deposited In formed ad-dimer rows atop the troughs of on the dimerised Si(001) surface (Figure 8.2). Deposition up to a 0.5 ML coverage on a surface held at a temperature above 423 K induced a two-domain 3x4-In reconstruction (E_e=45 eV), as shown in Plate 8.1(c).

Upon annealing the 300 K as-deposited Si(001)2x1-In surface to 573 K a slightly blurred 1x1 LEED pattern was observed (not shown). The LEED pattern of the annealed surface had a higher background intensity and the spots were broader than the original 2x1-In pattern. An increase in the Si KLL (92 eV) Auger intensity of about 10% accompanied this phase transformation, presumably
Plate 8.1  Photographs of LEED patterns
(a) (top photograph) clean Si(001)2×1 surface at an electron energy (E_g) of 65 eV,
(b) the Si(001)2×2-In reconstruction (E_g=70 eV), and
(c) the Si(001)3×4-In reconstruction (E_g=45 eV).

Refer to the text for the experimental conditions.
due to In desorption from the surface, or In migrating from the existing 2D layer to form 3D islands. The In-induced 1×1 LEED reconstruction was also observed by Kuwata et al. (1991) after annealing samples between temperatures of 373 K and 573 K.

8.4.3 SXRD Studies

The Growth of In on Si(001)

After in-vacuo cleaning of the Si(001) surface by annealing to 973 K followed by a flash to 1273 K sharp, intense fractional order diffraction peaks from the Si(001)2×1 surface reconstruction were observed indicating a well-ordered surface consisting of large reconstructed domains, an example of which was previously shown in Figure 4.10. This pattern was reproducible after many deposition and cleaning cycles.

The earlier AST curves (Figure 8.3) were grown on surfaces treated by flashing to a slightly lower temperature (1073 K) to remove the In and reconstruct the surface. The AST plots which were routinely recorded when monitoring growth by x-rays (and using a high temperature 1273 K flash between growth plots) were identical to the earlier results. X-ray measurements of the fractional order reflections from the clean surface, however, showed that the surface was less ordered when treated by lower temperature flashing, see Figure 8.4 which compares the (1.5, 0, 0.16) fractional order peak after flashing to (a) 1073 K and (b) 1273 K. The LEED patterns for the two flashing temperatures were indistinguishable. The SXRD measurements indicated that it was necessary to flash to 1273 K to fully reconstruct the surface. The growth mode determined in AST measurements is insensitive to ordering that can be detected in XRD, showing the greater sensitivity of SXRD compared to electron diffraction and Auger spectroscopy.

Indium was deposited on to the clean Si(001)2×1 surface at substrate temperatures of 300 and 373 K in order to investigate the dependence of the growth mode on temperature in the range where the (2×2)-In reconstruction occurs. Deposition at a higher temperature (523 K), inducing the formation of the 3×4 reconstruction, was performed as a comparison. The x-ray reflectivity and AES signal were simultaneously monitored as a function of deposition time.

Figure 8.5 shows the change in specularly reflected x-ray intensity when In is deposited on Si(001) at 373 K. The AST curve showed a break at a time corresponding to the completion of a monolayer as in the previous work.
Figure 8.4  Clean Si(001) (1.5, 0, 0.16) fractional order diffraction peak (a) after 1073 K flash with a FWHM of 0.20° and a height of 18 a.u., and (b) after 1273 K anneal giving FWHM of 0.02° and a height of 316 a.u.
Figure 8.5  Simultaneously measured AES and SXRD growth curves for the growth of In on Si(001) at (a) 373 and (b) 523 K.
(Section 8.4.1). The AST intensity fell to approximately 45% of the signal before opening the shutter. A single oscillation in the x-ray specular reflectivity was observed during growth monitored at (0, 0, 0.84) supporting a Stranski-Krastanov growth mode. In Figure 8.5 the break in the AST curve coincides with the intensity maximum of the x-ray reflectivity curve and coincident features between the x-ray and Auger curves has been previously observed during the growth of In on Si(111) by Finney et al (1992). Growth of In on Si(001) at 373 K is shown to be in a Stranski-Krastanov mode.

The growth of In on Si(001) at 300 K showed similar behaviour in the AST and x-ray intensity confirming a Stranski-Krastanov growth mode at room temperature.

Overlayer growth recorded at a substrate temperature of 523 K is shown in Figure 8.5(b). The AST curve showed a break at a coverage corresponding to monolayer completion and then levelled off. The AST intensity did not fall as low as in the above cases (dropping to about 70% of the initial intensity) confirming the trend observed in Figure 8.3. The x-ray intensity showed a minimum at about 6 minutes deposition time, similar to 373 K growth, but did not traverse the oscillation previously observed for growth at 373 K in Figure 8.5. A slight recovery in intensity (~5%) was achieved after the minimum after which the intensity continued at this constant level. A change in overlayer growth is suggested at this temperature. The quality of overlayer growth was worse and manifested itself as a smaller intensity drop in the AST signal. The AST plot still shows a sharp break indicating good formation at one monolayer. The behaviour is more strongly represented in the x-ray measurements which suggest that the first monolayer is incompletely formed before island growth begins.

In summary, the growth mode of In on Si(001) at 300 to 373 K follows a Stranski-Krastanov mode. At higher temperature the growth was less ordered and layer formation was somewhat inhibited, evident from the x-ray scattering measurements.

The Growth of Ga on Si(001)

The growth of Ga on Si(001) at substrate temperatures of 300 K and 373 K was studied using simultaneous AST and x-ray reflectivity measurements in comparison with growth of In under the same conditions. Figure 8.6 shows the x-ray reflectivity and Auger intensity monitored as a function of deposition time for Ga on Si(001) at the two different substrate temperatures, (a) 300 and (b) 373 K. In both cases the x-ray reflectivity was monitored at (0, 0, 0.84), near the anti-
Figure 8.6  The growth of Ga on Si(001) simultaneously monitored by AES and SXRD at substrate temperatures of (a) 300 K, and (b) 373 K. The y-scale of both curves is referenced to zero intensity.

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Bragg position for the Si(001). The chamber pressure during deposition was in the mid 10⁻¹⁰ mbar region. RBS analysis of the Ga covered surface showed no evidence of contamination. One monolayer of Ga was deposited in 15 minutes.

For Ga deposition at 300 K (Figure 8.6 (a)) the AST data showed no breaks and the x-ray intensity dropped sharply, again without any distinct features. This suggests a 3D growth mode for Ga on Si(001) at room temperature. At 373 K, however, the film showed improved layer growth suggested by the sharp break in the AST curve at a deposition time of about 6.5 minutes (Figure 8.6(b)), however, this did not correspond to the monolayer breakpoint (actually corresponding to ~0.43 ML of Ga). Interestingly, the measured x-ray intensity shows similar behaviour displaying a sharp break at the same stage of deposition. The initial drop in intensity indicates a roughening of the Si surface. The curve does not recover intensity indicating that a complete monolayer is not formed. Overall, the results indicate poorly ordered film formation.

The growth of Ga on Si(001) is less well-ordered than that of In at the same substrate temperatures. 3D island formation predominates at 300 K. At 373 K there is a tendency towards layer formation but breaks down before the completion of a single monolayer.

8.4.4 The Metal-Si(001) Interaction

Figure 8.7 shows a Si(001)2×1 fractional order reflection before and after (a) deposition of 1.7 ML of In at 300 K, and (b) deposition of 0.37 ML of Ga at 373 K. For In deposition at 300 K the integrated intensity of the peak was reduced to approximately 90 % of the initial value, indicating that the structure of the Si sublayer remained largely unchanged upon In deposition at 300 K. Northrup et al. (1991) proposed, from angle resolved photoemission spectroscopy (ARPES) measurements, that the In layer produced little disruption of the Si(001)2×1 surface. The FWHM (0.18°) of the fractional order peak was not significantly altered by In deposition, giving a correlation length of about 2594 Å and suggests that the In layer was disordered.

When Ga was deposited at the higher temperature of 373 K up to a coverage of 0.37 ML there was a reduction to about 63 % of the initial value (see Figure 8.7(b)) suggesting that the Si(001)2×1 surface reconstruction has been partly destroyed in contrast to the result for a significantly larger coverage of In (Figure 8.7(a)). Again, the FWHM of the peak was not significantly altered. If In or Ga replaced Si in the surface dimer structure (at the same height) we would anticipate an increase in the peak intensity due to the heavier mass of the adatom compared to
Figure 8.7  
(a) (0, 1.5, 0.16) fractional order peak before and after the deposition of 1.7 ML of In at 300 K, the FWHM of $-0.018^\circ$ (corresponding to a correlation length of 2594 Å) and the intensity are not significantly changed. (b) (1.5, 0, 0.16) fractional order peak before and after the growth of 0.37 ML of Ga at 300 K, the FWHM of $-0.013^\circ$ (giving a correlation length of 3592 Å) is unchanged, but the intensity of the peak falls to 63% of initial value.
Si. The AST and x-ray data on the growth mode of Ga on Si would suggest that the adsorbate-covered surface is quite disordered. The atomic radius of Ga (1.22 Å) is considerably smaller than that of In (1.63 Å) and Ga atoms may penetrate deeper into the Si surface disrupting the structure at the elevated temperature.

Since the substrate temperature is different in each case a direct comparison would not be appropriate; the role of temperature needs to be defined before a firm conclusion can be reached. In Figure 8.8 the (1.5, 0, 0.16) fractional order reflection is monitored during the deposition of In at 373 K, comparable to Figure 8.7(b) for Ga deposition, and shows a fall in intensity as for Ga. We therefore conclude that the substrate temperature, not the adsorbate species, determines the behaviour of the Si(001) surface during metal deposition.

8.4.5 The Si(001)2×1-In Surface Reconstruction

From the surface phase diagram for In (Figure 8.1) the Si(001)2×1-In phase exists over a coverage range of 1 to 3 ML and at a substrate temperature below 423 K. From LEED observations the overlayer possesses the same symmetry as the Si(001)2×1 surface, however, the poorer quality of the LEED pattern for the metal covered surface suggests a higher amount of disorder. It is difficult to gain further information about the surface morphology from (qualitative) LEED studies and the exact behaviour of the In adatoms on the surface can only be hypothesised. For example, the deposited adatoms may merely roughen the clean Si(001) surface leaving the substrate reconstruction largely undisturbed, or form an ordered overlayer with the same symmetry as the original surface destroying the Si reconstruction.

To gain qualitative information about the metal-induced Si(001)2×1-In reconstruction SXRD was employed. The 2×1-In phase was formed by deposition of 1.0±0.05 ML of In at a substrate temperature 373 K. To derive information on the metal adatom interaction with the Si(001)2×1 surface the (1.5, 0, 0.16) fractional order peak from the clean surface reconstruction was monitored as a function of deposition time. Figure 8.8 shows the intensity of the (1.5, 0, 0.16) fractional order reflection during In deposition at 373 K. During formation of the Si(001)2×1-In phase the intensity of the peak initially decreased, reaching a minimum at a coverage of ~0.5 ML, after which a small intensity gain was observed. We interpret the decrease in the fractional order intensity as the destruction of the Si dimers by the incoming In atoms. Above a coverage of 0.5 ML the intensity increases due to the formation of In dimers, although not forming a complete structure. This is an important result indicating that the 2×1 structure observed at a 1 ML coverage is due to an ordered In surface rather than
Figure 8.8 (a) Growth of the Si(001)2×1-In reconstruction monitored as a function of deposition time on the Si(001) (1.5, 0, 0.16) fractional order peak. 1.01±0.05 ML of In was deposited at a substrate temperature of 373 K. The dashed line indicates the start of deposition, (b) the (1.5, 0, 0.16) fractional order before and after deposition (i) FWHM of 0.026°, integrated intensity is 25.95 a.u., (ii) FWHM of 0.027°, the integrated intensity is 4.96 a.u.
the persistence of the substrate reconstruction and indicates that Si dimers are replaced by In dimers. The existence of a 2×1-In phase at a coverage of 1 ML was confirmed, but the surface was disordered.

Figure 8.8(b) shows a transverse scan through the fractional order peak before and after deposition from which the FWHM can be found. The FWHM remains virtually unchanged upon deposition (giving a correlation length of ~1850 Å), indicating that the size of the reconstructed domain for the 2×1-In phase was the same. The 2×1-In phase is not complete and the In overlayer must adopt other structures to account for a total coverage of 1 ML, for example a 1×1-In structure, or 3D islands. Point defects may also be present.

The (2, 0, t) integer order rod was measured for the In-covered surface (see Figure 8.9) to determine the perpendicular structure of the adsorbed metal layers. The surface was found to be disordered (σrms was typically 1.5 to 2.5 Å). In the analysis a better fit was obtained with In dimers at the surface giving χ² values of 3.0 and 2.0 respectively by In dimers in the same geometry, supporting the conclusions from the in-plane data.

When In was deposited on the Si(001) surface the Si dimers were replaced by In dimers causing a strain in the surface and subsurface layers, mainly due to the different size of the In atoms, reducing the intensity of the fractional order peak from the 2×1 reconstruction. Initially, the In dimers formed in isolated areas at random locations on the surface producing significant strain, but as the coverage increased the individual areas coalesced until a complete layer is achieved at a coverage of 1 ML and the overall strain was reduced, detected as an increase in the peak intensity. If all the Si dimers were replaced by In dimers (at the same atomic co-ordinates) we would expect a significant increase in the diffracted intensity, from the respective atomic numbers. This was not observed. The surface was disordered. Reconstruction of subsurface layers contributes to the fractional order peak intensity and the presence of In dimers may cause a relaxation of these layers and, in consequence, cause a reduction in the intensity.

From previous experience it was found that the Si surface requires heating to 1273 K to induce a highly ordered 2×1 surface reconstruction. It is hardly surprising that quality of the 2×1-In phase is poor. Although growth was performed at an elevated temperature (373 K) there was insufficient energy to induce ordering of the adatoms. Besides, the 2×1-In phase does not exist above 423 K and In is completely desorbed from the surface at 800°C and therefore a higher quality reconstruction could not be prepared this way. The proposed overlayer structure is illustrated in Figure 8.10.
Figure 8.9 (2, 0, l) rod scan for 1 ML In/Si(001) modelled by Si dimerised surface (dashed line) and In dimerised surface (solid line) ($\chi^2$ of 3.02 and 1.99 respectively), bulk Si (dotted line).
In conclusion, In dimers replace Si dimers during the formation of the Si(001)2×1-In phase at a coverage of 1 ML, but the surface is disordered.

8.4.6 The Si(001)2×2-In Reconstruction

The metal induced Si(001)2×2-In reconstruction (see Figure 8.2) exists over a coverage range of 0.3-0.5 ML at a substrate temperature between 300 and 423 K. The structure has been observed by LEED measurements in this and other studies (Knall et al 1986) suggesting that the surface was well ordered. Attempts were made to determine the exact structure of this reconstruction using x-ray scattering, however, the Si(001)2×2-In surface reconstruction could not be measured by SXRD. In reality it would appear that the 2×2-In reconstruction has a small correlation length, certainly smaller than that measurable by SXRD, although within the detection limits of LEED. The structure is presumably quite disordered with only small sized reconstructed domains.
Figure 8.10  Schematic diagram of (a) clean the Si(001) surface showing a 2x1 unit cell (dotted line), and the extent of a reconstructed domain (dashed line), (b) proposed surface after deposition of In at 373 K, a few Si dimers still remain, In dimers replace Si dimers, In forms a 1x1 structure also, generally disordered.
8.5 Conclusion

The techniques of SXRD, LEED and AES were used to investigate the growth mode and metal-induced surface reconstructions of In and Ga on Si(001) at sub-monolayer and monolayer coverages. For In at all deposition temperatures (300 to 623 K) the growth was in a Stranski-Krastanov mode. Ga exhibited 3D island formation at 300 K, but better layer formation at 373 K. The overlayer structure and growth behaviour had a dependence on the substrate temperature. The AST results suggested that the sticking-coefficient of In to the clean Si surface was independent of temperature up to a coverage of 1.0 ML, even at high temperature (623 K). Experimental results indicated significant In desorption from the Si surface during deposition at a substrate temperature of 673 K preventing any prolonged and ordered overlayer growth. LEED investigations showed a sharp, two-domain 2x1 pattern for the clean Si(001) surface. A Si(001)2x2-In reconstruction was induced after deposition of In at a substrate temperature below 423 K up to a coverage of 0.5 ML. A 2x1-In pattern was observed after growth of 1 to 2 ML of In on the clean Si surface at deposition temperatures up to 423 K. Upon annealing the as-deposited sample to 573 K, a 1x1 LEED pattern appeared. Deposition at a substrate temperature above 423 K to a coverage of 0.5 induced a 4x3-In pattern.

The Si(001)2x2-In surface reconstruction could not be measured using SXRD although LEED measurements in this and other studies (Knall et al 1986) suggested that it was weakly ordered. In reality it would appear that the 2x2-In reconstruction has a small correlation length, certainly smaller than that measurable by SXRD, although within the detection limits of LEED. The structure is presumably quite disordered with only small reconstructed domains.

Carbon contamination was shown to induce disordered overlayer growth.
Chapter 9
Summary and Suggestions for Future Work

9.1 Summary

This chapter contains a summary of the results presented in the previous experimental sections discussed in the light of other studies. The in-situ techniques used to conduct the experimental work included surface x-ray diffraction (SXRD), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES), whilst scanning electron microscopy (SEM) and Rutherford back scattering (RBS) measurements were performed ex-situ. Section 9.2 deals with the growth and atomic structure of metastable fcc Fe (γ-Fe) films, grown by molecular beam epitaxy (MBE) on Cu(001), studied as a function of Fe coverage and substrate temperature. Investigations into phenomena such as the temperature dependence of the growth mode, Fe-Cu intermixing in the interfacial region, and relaxation to bcc Fe (bulk) phase were carried out. Changes in the interlayer spacing at the surface of the film were observed as a function of coverage. Section 9.3 summarises the growth of the metastable bcc phase of Co on the decapped GaAs(001)4×1 reconstructed surface. A comparison with the growth of Fe on the same surface is also reported. In Section 9.4 the growth of In and Ga on the technologically important Si(001) surface is summarised, with emphasis placed upon the interaction of the metal adatoms with the dimerised Si(001)2×1 surface reconstruction, as well as determination of the growth mode. For the Si(001)2×1-In reconstruction, measured at one monolayer (ML) coverage, Si dimers were replaced by In dimers. The reader is referred to the relevant chapters for a more comprehensive discussion of the experimental results. Finally, suggestions for further experimental work are made in Section 9.5.

9.2 The Growth and Atomic Structure of Fe on Cu(001)

Monitoring layer formation on an atomic scale using SXRD is a proven method for determining overlayer growth modes (see, for example, Finney et al 1992, Vlieg et al 1988). The technique is especially powerful in cases where well-ordered layer growth predominates, as in the case of Fe on Cu(001) (James et al 1994). The technique provides much structural information in addition to a simple determination of the growth mode. Coincident features in the simultaneously measured data by SXRD and AES can be directly correlated

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(Finney et al. 1992) illustrating the superior sensitivity of x-ray scattering to atomic growth.

The growth and atomic structure of epitaxial Fe films on Cu(001) was studied as a function of substrate temperature and Fe coverage in chapters 5 and 6. The growth mode was determined from the intensity variation of the x-ray reflectivity at a fixed point in reciprocal space during overlayer growth. Growth at 85 K was diffusion limited, indicated by a rapid fall in the specular intensity at the early stages of deposition. At 300 K, well-defined parabolic intensity oscillations were observed clearly showing a single layer-by-layer growth mode, consistent with kinematical theory. These data are in disagreement with previous studies (see, for example, Dastoor 1992, Steigerwald 1988). A bilayer-by-layer growth mode at 300 K, suggested by Glatzel et al. (1991), can be discounted from measurements as a function of perpendicular momentum transfer during growth. The difference, albeit small, in the atomic scattering factors allowed confirmation of intermixing between the Fe overlayer and first Cu sublayer during the initial stages of deposition, as proposed by Chambliss and Johnson (1994). At elevated substrate temperatures the effect of Fe-Cu interdiffusion became more pronounced and poor layer growth ensued.

The atomic structure of the clean Cu(001) and adsorbate-covered surface at coverages of 1, 2, 4 and 6 ML was determined from the measured intensity variation perpendicular to the sample surface using kinematical analysis. The Cu(001) surface relaxations were in good agreement with previous studies (Davis and Noonan 1982) and no surface reconstruction was observed. Fe-Cu atomic intermixing was included at the overlayer-substrate interface improving the fit to the measured data. The magnitude and direction of interlayer spacing at the surface of the film was dependent on film thickness. Structural and magnetic changes in the film strongly influence each other and the expanded layer structure of the film can be linked with the unusual magnetic behaviour observed in ultrathin fcc Fe films grown on Cu(001) by MBE (Zillgen et al. 1994).

9.3 The Growth of Co and Fe on GaAs(001)

A GaAs(001)4×1 surface reconstruction was obtained after removal of the amorphous-As (α-As) cap in UHV. The stages of the desorption process proposed by Resch et al. (1992) could be identified in the x-ray reflectivity curve measured during thermal desorption. From the fractional order diffraction peaks associated with the GaAs(001)4×1 reconstruction the correlation length was determined to be ~1160 Å.
Deposition of Co on the GaAs(001)4×1 surface caused substrate disruption giving intermixing of metal and substrate species with inclusion of As and Ga atoms in the metal film and As surface segregation. The measured x-ray intensity variation during deposition indicated poorly ordered overlayer growth, with eventual coalescence of the individual Co islands at a coverage of ~8.5 ML. The vertical morphology of the Co film, determined from specular rod data, was consistent with the metastable bcc Co structure.

Annealing a 50 ML thick Co film for 7.5 minutes at 773 K altered the film structure. Interference fringes observed for the as-grown Co film disappeared, implying roughening and disruption of the film. Desorption of atomic species may also have occurred at this temperature. An additional peak appeared in the specular rod after annealing corresponding to hcp Co islands.

The growth of Fe on the decapped GaAs(001)4×1 surface behaved in a similar manner. Deposition of Fe at 300 K caused disruption of the substrate with diffusion and surface segregation of the substrate species, but to a lesser extent than in the case of Co. The formation of Fe layers was better ordered.

9.4 The Growth of In and Ga on the Si(001)2×1 Surface

The interaction of In and Ga with the technologically important Si(001) surface was reported in chapter 8. Detailed AST studies for In on Si(001) showed a Stranski-Krastanov growth mode at all substrate temperatures. X-ray intensity growth curves for In showed, at most, one complete intensity oscillation confirming the Stranski-Krastanov growth mode. Ga overlayer formation was more disordered showing a 3D growth mode at 300 K, but improved overlayer growth at 373 K. At 300 K the deposited In adatoms had little effect on the underlying 2×1 Si reconstruction, whereas In and Ga strongly interacted with the clean surface reconstruction at a deposition temperature of 373 K, significantly diminishing the intensity of the associated fractional order reflections.

Previous work showed that the deposited metal atoms form ad-dimers above the Si(001)2×1 reconstructed surface (Baski et al. 1991). Coverage and temperature dependent metal-induced surface reconstructions were reported for In on Si(001) from LEED investigations. The Si(001)2×2-In surface reconstruction could not be measured using SXRD, although the reconstruction appeared to be well-ordered from electron diffraction studies. This suggests that the structure is poorly reconstructed consisting of small, isolated (uncorrelated) 2×2-In domains with a
small correlation length (LEED typically measures hundreds of Å of the surface reconstruction, whereas SXRD samples thousands of Å of the surface and a better quality surface reconstruction is required).

The Si(001)2×1-In reconstructed was formed at a coverage of 1.0 ML. During growth the intensity of the (1.5, 0, 0.16) fractional order peak from the Si(001) reconstruction was monitored. The dimerised Si surface was largely destroyed by the deposition of In, but an increase in surface ordering was observed at a coverage of 1 ML, presumably due to the formation of In dimers, which replaced the Si dimers. Out of plane measurements were consistent with surface In dimers, however, the surface was quite disordered and other structures were also present.

9.5 Suggestions for Future Work

SXRD is an efficient method for monitoring the qualitative aspects of epitaxy and accurately determining the specific properties of layer growth and the atomic structure of the resulting phases. The advent of higher intensity and higher brilliance synchrotron sources, for example, the European Synchrotron Radiation Facility (ESRF) in France, enables investigation into more subtle phenomena and effects which occur on a rapid time scale. For example, diffuse scattering provides information about island size and distribution but, by its very nature, is weak and requires an high brilliance source to efficiently measure the scattering. An overall improvement in the experiment counting statistics is a direct consequence. A comparison of the synchrotron radiation source (SRS) beam line station 9.4 is made with stations at the ESRF in Table 9.1. BL7 at the ESRF offers two orders of magnitude more intensity than wiggler beam line station 9.4 at the SRS.

An investigation of epitaxially formed metastable phases is an obvious area in which SXRD could be extensively applied. The technique of SXRD is especially powerful when the overlayer and substrate atoms differ significantly in atomic number \(Z_{\text{overlay}} > Z_{\text{substrate}}\) and film formation proceeds in a well-defined manner. The interfacial structure and, in particular, the adsorbate-induced strain resulting from the epitaxial growth of one crystal structure on another, can be accurately determined using SXRD (Williams et al 1991), unlike other (electron-based) techniques which are only capable of probing the topmost surface layers.
The room temperature growth of Fe on Cu(001) has been widely studied and much is understood about the growth mode and overlayer structure. A complementary study at low temperature (LT) to fully determine the growth mode and film morphology, in particular, the development of the metal island size and separation as a function of coverage, will build on the initial results presented in this thesis. Fe growth on Cu(001) at 85 K displayed markedly different behaviour with predominantly diffusion limited growth (James et al 1994). Fe-Cu intermixing is expected to be less significant at lower temperature with the formation of the bulk bcc Fe phase occurring earlier, suggested by the rapid breakdown of epitaxial growth at 85 K, although no evidence was found for the formation of the bcc Fe phase at a coverage of 4 ML from our results. Recently, considerable interest has been shown in Fe films grown at LT on Cu(001) and annealed as a method to reduce intermixing and fabricate better quality films.
Another aspect that can be explored with a higher intensity source is the effect of deposition rate on the initial growth behaviour. Measurements at Daresbury Laboratory were restricted to slow deposition rates (typically 15 minutes ML⁻¹) by the limited intensity of the source. To simulate the conditions used in the commercial MBE growth chambers deposition rates of 1 ML in 10 s must be used, requiring exploitation of the superior intensity of the ESRF to give good statistics. Previous work carried out at faster deposition rates (2 min ML⁻¹) at the SRS, although poor statistics, showed evidence of an alternative growth behaviour indicating that growth is kinetically dependent. Investigation of such effects may explain the many differences reported in the literature arising from different effective growth rates.

Co, Fe, and Cr exhibit interesting magnetic behaviour when epitaxially grown on oriented substrates. An extension of the work in this thesis is to investigate the epitaxial growth of Cr on the (001) face of GaAs. The growth behaviour is expected to be similar to that of Co and Fe.

The main areas of interest in the metal/Si(001) systems are those of low coverage and low temperature where the metal is most strongly influenced by the clean Si surface. In order to determine the structure of the Si(001)2×2-In reconstruction at 0.5 ML deposition of In on a vicinal (001) surface of Si (typically a 4° miscut) is required to induce a predominantly single domain reconstruction. The growth of As on Si(001) and the interaction of this metal with the substrate, would allow comment to be made on the epitaxy of GaAs on Si. General trends for metal growth on Si(001) could be put forward.

From a technical point of view on beam line station 9.4, the out-of-plane detection system will increase the accuracy of measurements because a larger amount of reciprocal space can be sampled.
Appendix A

Sample Cleaning

A.1 Procedure for Cleaning Silicon Substrates before UHV Processing

The method described here is a modification of that developed by Finney (1992) after private communication with J.M.C. Thornton.

Residual contamination of silicon substrates inherent in wafer production has proven difficult to remove in the past (Henderson 1972). The following procedure is a hybrid of the wet chemical processes that have appeared in the literature over the past 20 years (Kern 1984, Henderson 1972, Ishizaka 1986, Woolf 1989, Thornton 1989, Suemitsu 1989, Kaneko 1989), in particular, the RCA process.

All chemicals used in this process are electronic grade, e.g. BDH "ARISTAR" grade chemicals, and ultra-clean deionised water with a resistivity of 18 MΩ or better at 20°C is used. All procedures must be carried out in a dedicated fume cupboard set up in clean conditions and the workers must be fully versed with the safety precautions (see relevant COSHH forms, etc.) required when handling concentrated acids, particularly hydrofluoric acid (HF). The dedicated vessels and tweezers are made from perfluoralkoxy (PFA) and the beakers from fused silica.

1. Degrease

The sample should be thoroughly degreased in an ultra-sonic bath of propan-2-ol (IPA) for at least 15 minutes. PYREX beakers, ultra-sonically cleaned in IPA, are used for this procedure. Transfer the sample to a clean FLUOROWARE box, using dedicated PTFE tweezers only, after degreasing.

2. Removal of Residual Organic Contamination and Certain Metals

(i) Preparation of a FRESH solution of H₂O: NH₄OH: H₂O₂ (5: 1: 1).

Firstly mix the H₂O and NH₄OH in a FUSED SILICA beaker and place on a hot plate to raise the mixture to 80°C. Just before the sample is dipped in add the H₂O₂. Place the sample in the mixture, using PFA tweezers, for 10 minutes. Bubbling will occur due to the evolution of oxygen. Do not allow the mixture to boil as the H₂O₂ will decompose.
(ii) Remove the sample with the tweezers and rinse in water.

3. Stripping of the Thin Hydrous Film

(i) Prepare a 5% solution of HF, i.e. a mixture of HF: H₂O (1: 10), in a PFA beaker. Using PFA tweezers submerge the sample in the solution for 30 seconds. On removing the sample from the solution the exposed silicon (but not SiO₂) will repel the HF.

(ii) Rinse the sample in deionised water for 30 seconds to remove the HF. The water also soaks up all surface dangling bonds stopping any carbonic contamination (Suemitsu 1989) or regrowth of the hydrous oxide film (Kern 1984).

4. Removal of remaining atomic and ionic contamination and the formation of a "clean" protective oxide film

(i) Transfer the sample directly from the previous step, without drying, into a FRESHLY prepared solution of H₂O: HCl: H₂O₂ (6: 1: 1). Again, prepare the H₂O and HCl in advance in a FUSED SILICA beaker and heat to 80°C, adding the H₂O₂ just before dipping the sample.

(ii) Heat the sample in the solution at 80°C for 15 minutes.

(iii) Remove the sample and rinse in deionised water.

(iv) Hold the sample firmly with PFA tweezers on a clean room wipe and dry in nitrogen gas from a filtered gas gun.

(v) Store the dried sample in a FLUOROWARE box that has been previously cleaned with good quality deionised water and blown dry with filtered nitrogen gas.

In vacuo sample preparation consists of two electron beam heating cycles, annealing at 700°C for 5 minutes, and flashing at 1000°C for 2 minutes to remove the protective oxide layer, followed by a slow cool down (at a rate of 1°C s⁻¹) to RT. All sample temperatures above 500°C are measured with a calibrated IR pyrometer as described elsewhere (Finney 1992). The typical power supply requirements for the annealing and flashing cycles are a filament current of 3.2 Amps, with an emission 15 mA (at 700°C) and 3.8 Amps, with 35 mA (at 1000°C), for an applied (positive) potential of 1 kV. The maximum pressure reached
during this cleaning process is less than $1 \times 10^{-9}$ mbar, soon recovering to the $10^{-11}$ mbar range. Such UHV conditions must be attained in order to produce contamination free silicon surfaces. For thoroughly outgassed sample heaters it has been known for the pressure to remain in the $10^{-11}$ mbar range during the flashing cycle.

Use the samples as soon as possible as the protective oxide film degrades with increased exposure to air (Kern 1984).

A.2 Preparation of Gallium Arsenide Substrates

WARNING: GaAs is POISONOUS and must be HANDLED WITH CARE. Wear GLOVES, PROTECTIVE CLOTHING, and a FACE MASK. All materials must be DISPOSED OF SAFELY. Refer to the COSHH regulations BEFORE handling GaAs wafer.

Preparation of capped GaAs(001) wafer (DRA Malvern)

A commercial GaAs(001) wafer was successively cleaned in trichloroethylene, methanol, hydrofluoric acid, deionised water and dried before loading into a MBE system at DRA, Malvern (Johnson). In vacuo cleaning consisted of Ar ion bombardment and annealing cycles to reduce contamination prior to loading into the main MBE growth chamber where the wafer was annealed to produce a c(2×8) surface reconstruction, as observed by reflection high energy electron diffraction (RHEED) upon which a 3000 Å GaAs(001) epilayer was grown by MBE, and immediately capped with a thin amorphous-As (α-As) layer (a few hundred Å thick).

Commercial GaAs wafer is too thin (~0.5 mm) to have steps cut in its edges it is bonded, by a technique commonly used in the MBE industry known as indium bonding, to a Mo block which can then be mounted on the sample heater in the standard way. The complete procedure is described in detail below. All tools used had been cleaned in ultrasonic baths of acetone and methanol, and then dried.

1. Cutting the GaAs wafer

The GaAs wafer was first cut into $8 \times 8$ mm$^2$ pieces. The wafer is placed with the α-As capped (dull) side upwards on a lint-free tissue and pressure applied at the edge of the wafer with the tip of a scalpel blade. The wafer will cleave cleanly along the two intrinsic crystal planes, the direction of which are indicated by the
flats on the wafer edges. The procedure is repeated until the original size wafer is reduced to 8\times 8 \text{ mm}^2 sections.

2. Preparation of the Mo backing plate

The Mo block, of dimensions 8\times 10 \times 1 \text{ mm}^3, was successively cleaned in ultrasonic baths of detergent with hot water, acetone, and methanol, rinsing between each stage and finally drying. The Mo block was then electropolished (Gardiner 1983) and annealed by RF heating in a vacuum of \sim 10^{-7} \text{ mbar} to \sim 800^\circ \text{C} to outgas it for compatibility with the UHV environment. The surface of the Mo block was lightly scratched, using a suitably sharp clean tool, to aid adhesion of In to the surface of the block.

The following mounting procedure is carried out in a FUME CUPBOARD to prevent inhalation of TOXIC ARSENIC VAPOUR.

3. In-bonding of the GaAs wafer to the Mo block

The Mo block is put on the hotplate, the temperature of which is monitored by a chromel-alumel thermocouple, and allowed to heat up to about 150^\circ \text{C} (the melting point of In is 156.8^\circ \text{C}). A very small piece of In (99.99999\% purity) was placed on the surface of the Mo block and, once molten, was thinly spread across the surface of the block using a scalpel blade.

A piece of GaAs wafer was placed onto the block and carefully moved around the surface in order to completely wet the underside of the wafer. A visual inspection of the wetting may be made by carefully lifting the wafer by one edge to check if the underside is evenly coated with In. The bonded substrate was allowed to cool to room temperature.

4. In-vacuo treatment

The bonded sample mimics a typical SXRD sample and can be mounted on the sample heater in the standard way. In-vacuo treatment involved removal of the \alpha-As cap to retrieve the clean, well-ordered reconstructed GaAs(001) surface. The sample is heated to \sim 500^\circ \text{C} at UHV to thermally desorb the \alpha-As cap. Desorption of the cap is accompanied by a brief pressure burst in the chamber as the main part of the cap is blown off. After desorption the mirrored surface of the MBE grown epilayer is exposed.

Details of the resulting clean GaAs(001) surface can be found in Chapter 8.
Appendix B

Publications

The Growth and Atomic Structure of the Si(lll)-Indium Interface Studied by Surface X-ray Diffraction

A Surface X-ray Diffraction Study of the Growth of Ultrathin Fe Layers on Cu(OOl)

A Surface X-ray Diffraction Study of the Si(lll)-Pb Buried Interface

Oxygen Modified Growth of Gd on Mo(ll0)
S. Mozley, C.L. Nicklin, M.A. James, P. Steadman, C. Norris, and M. Lohmeier.

Influence of Interfacial Atomic Structure on the Schottky Barrier Height of Si(lll)-Pb

The Pseudomorphic Growth and Atomic Structure of Ultrathin Fe Layers on Cu(001) Studied by Surface X-Ray Diffraction
In preparation. To be submitted to Phys. Rev. B.

The Growth and Atomic Structure of 3d Metal Films on GaAs(001)
A Surface X-ray Diffraction Study of In Growth on Si(001)

Reports

Resonant Photoemission Study of the Rare Earth Tm

The Atomic Structure of the Si(111)4×1-In Reconstruction
M.S. Finney, C. Norris, P.B. Howes, M.A. James, A.D. Johnson, and J.E. Macdonald.

Metallic Growth on Si(001) Studied by Surface X-ray Diffraction
P.B. Howes, M.A. James, M.S. Finney, C. Norris, A.D. Johnson, and E. Vlieg.

Epitaxial growth of Fe on Cu(001)

A Surface X-Ray Diffraction Study of the Growth of In and Ga on Si(001)
M.A. James, C. Norris, C.L. Nicklin, J.S.G. Taylor, M.S. Finney, and W.J. Huisman.

Oxygen Modified Growth of Gd on Mo(110)
S. Mozley, C.L. Nicklin, M.A. James, P. Steadman, C. Norris, and M. Lohmeier.

Stabilisation of 3d Metals on GaAs(001)
References


Auger, P., J. Phys. Radium, 6 (1925)


Darici, Y., Marcano, J., Min, H., Montano, P.A., to be published (1987??)


James, R.W., The Optical Principles of the Diffraction of X-Rays (Ox Bow, Connecticut, 1982).


Jeynes, C., and Chan, C.W.M., RBS analysis, Department of Electronic and Electrical Engineering, University of Surrey, Guildford, Surrey, GU2 5XH, UK.


Johnson, A.D., GaAs(001) substrates provided and prepared by MBE at DRA Malvern, UK.


Koper, R.J.I.M., Si(001) substrates polished at the FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ, Amsterdam, The Netherlands.


McTurk, G.L.C, SEM performed at Leicester University.


Norris, C., J.S.G. Taylor, P.R. Moore, N.W. Harris, and M. Miller, *Daresbury Annual Report* (1986/7) 124, also Norris, C., J.S.G. Taylor, P.R. Moore, N.W. Harris, and M. Miller, to be published.


Samples cut at the Materials Centre at the University of Birmingham.


