INTERFACIAL EFFECTS ON THE STRUCTURE OF THIN METAL FILMS

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DISSENTATION
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ABSTRACT

Three studies of thin metal films grown on semiconductor and insulator substrates are presented. Thin films grown on a substrate decorated by a periodic array of atomic wires can exhibit unusual properties such as stacking faults and electronic topological phase transitions due to the interfacial modulation. We report a study of Ag films grown on an array of atomic In chains on Si(111). Prior STM studies have suggested an array of stacking faults in the Ag films that allow the film lattice structure to match the interfacial modulations. STM however can only probe the surface. Our work uses x-ray diffraction to elucidate the internal 3-dimensional structure of this system. The measurements are found to be best explained by a model in which the unit cell contains a single stacking fault.

When the thickness of a thin film approaches the nanoscale significant changes in its properties can occur known as quantum size effects. Bilayer oscillations in the preferred island heights as a function of thickness in Pb films grown on Si(111) substrates is one example of a quantum size effect that is now well understood. Here we present a study of Pb films grown on sapphire substrates and present evidence of quantum size effects in a metal on insulator system. Intriguing difference between the Pb on Si system and this system are observed. The crossover between preferences for even and odd thicknesses is not observed in this system, over the range of thicknesses studied, as they are in the
Pb on Si case. The preferred heights are found to have much greater thermal stability demonstrating a connection between the quantum growth of thin films and the substrate band gap.

By growing thin films from materials with substantially different electronic properties interesting changes in the quantum growth behavior should also be observable. In the third study reported surface x-ray diffraction experiments on In films grown on Si substrates are presented. In films are grown on \( \text{Si}(111)-(7\times7) \) and \( \text{Si}(111)-(\sqrt{3}\times\sqrt{3})\)-In substrates. The \( \text{Si}(111)-(7\times7) \) surface is found to persist upon burial by the film. Although preferences for island heights at low coverages have been observed no observation of preferred island heights above 7 monolayers (ML) have been made in previous studies of this system. Our experiments show that by annealing the sample a preference for islands 13 ML in height can be seen.
To my wife Sung Hee
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LIST OF ABBREVIATIONS

AFM  atomic force microscope
APS  Advanced Photon Source
bct  body-centered-tetragonal
CCD  charge coupled device
CTR  crystal truncation rod
fcc  face-centered-cubic
MBE  molecular beam epitaxy
ML   monolayer
QSE  quantum size effect
RHEED reflection high energy electron diffraction
r.l.u. reciprocal lattice unit
STM  scanning tunneling microscope
SXRD surfaces x-ray diffraction
TDS  thermal diffuse scattering
TSP  titanium sublimation pump
UHV  ultra high vacuum
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\[ \frac{d\sigma}{d\Omega} \quad \text{Scattering cross section of an electron} \]

\[ t \quad \text{Time} \]
CHAPTER 1

INTRODUCTION

As the size of a system approaches the wave length of an electron its properties often diverge significantly from those of its bulk counterpart. Such changes in systems properties are known as quantum size effects (QSEs). The sizes of features in technological devices are beginning to shrink to scales in which these effects can no longer be ignored making it increasingly important to understand the properties of systems with these dimensions. In particular developing techniques to tune the electronic and atomic structures of these systems will be crucial in developing devices on such a scale.

Ultrathin films provide an interesting possibility to study some of these quantum size effects. These systems have nanometer scales in one dimension but have bulk like dimensions in the other two directions. They are structurally quite simple and relatively easy to fabricate compared to some other structures with nanometer scales in three dimensions however many interesting QSEs can be observed in these systems. In the case of thin metal films grown on semiconductor or insulator substrates the electrons in the metal film are confined by the substrate interface and the vacuum at their surface. A great deal of work has gone into studying such systems and a plethora of QSEs, resulting from this confinement, have been observed. Changes in properties, due to confinement, such as electron density, transport properties, electron phonon coupling, layer relaxations, thermal
stability, surface energy and superconducting transition temperature have been studied [1-13]. There are a variety of ways in which to tune the properties of these systems, they can be sensitive to temperature, chemical composition and the structure and orientation of the interface among other parameters. A final advantage of studying thin films is that the large lateral dimensions make these systems available to techniques in which data is collected from a large area of the surface simultaneously.

The primary experimental technique used in this thesis is surface x-ray diffraction (SXRD). Unlike scanning probe techniques which generally provide information over only a small portion of the surface SXRD can provide statistical information concerning the films structure over a large area of the surface. Although many techniques used for studying surface science are sensitive to only the top layers of a thin film the large penetration depth of x-rays means that this technique can render information about the internal structure of the film and its interface. Because of this x-rays interact very weakly with surfaces and so x-ray diffraction was once considered unsuitable for studying surface science. Synchrotron sources have since been developed which can generate a high enough flux of x-rays so that surface scattering can be easily observed making experiments, which were once seen as impractical, routine.

As is the case with most dissertations this thesis consist of two parts. Chapters 2 and 3 present background information that is relevant to the research described here. Chapters 4, 5 and 6 describe the experimental work and analysis
which was carried out in the research projects described here and present the results and conclusions drawn from these projects.

In chapter 2 the formalism for x-ray scattering is developed. First the basic formalism and conventions for describing crystals and surfaces is given. Starting from scattering from a single electron the formulas necessary to describe scattering from a bulk crystal are motivated. Then scattering from 2 dimensional samples is discussed. Finally a model which can actually describe the data collected in a SXRD experiment on thin films is rendered.

In chapter 3 some of the experimental techniques and equipment used to carry out the research involved in this thesis is discussed. A discussion of synchrotrons and the way that x-rays are generated and detected in this work is presented. The techniques and equipment used to generate an ultrahigh vacuum (UHV) environment and for surface preparation and characterization are described.

In chapter 4 a description of a SXRD experiment done on Ag films grown on the Si(111)-(4×1)-In surface is presented. Experiments carried out using a scanning tunneling microscope (STM) have shown that these films are modulated by the underlying interface with the same periodicity and it has been suggested that a stacking fault running through the film allows the periodicity of this modulation to match that of the substrate [14]. Models involving one and two stacking faults have been proposed. Our SXRD work shows that the films are consistent with the single stacking fault model.
In studying quantum size effects Pb films grown on Si substrates have been a model system and a great deal of research has been done on this system. Among the many quantum size effects that have been observed in this system, Pb islands of certain heights have been shown to be preferred over islands with other heights. In chapter 5 a study of Pb films grown on sapphire substrates is presented. This study reveals many similarities to the Pb on Si case but some important differences are also found highlighting how the substrates role in confining the electrons in a thin metal film can affect the films properties.

In chapter 6 a preliminary study of In films grown on Si substrates is presented. Quantum size effects are suggested to be present in this system. In films are grown on both the Si(111)-(7×7) and the Si(111)-$\left(\sqrt{3}\times\sqrt{3}\right)$-In surfaces and the growth of the films is found to be significantly affected.

Finally in chapter 7 the conclusions of this body of research are summarized.

REFERENCES


CHAPTER 2
THEORY OF X-RAY DIFFRACTION

2.1 INTRODUCTION

The focus in the study of condensed matter physics has throughout its history held a strong bias towards systems with a crystal lattice structure. The underlying symmetry of these systems can be exploited to allow a level of understanding that would not otherwise be possible. The reason why so many systems have a crystal lattice is not fully understood however it can be stated that an arrangement of atoms which is energetically favorable in one part of a system is likely to be favorable in another part of the system. In the early sections of this chapter the formalism used to describe the structure of bulk and surface systems as well as thin films will be briefly discussed as it will be extremely important for the discussion of x-ray diffraction.

In the remaining sections of this chapter the formalism for x-ray diffraction will be built starting with diffraction from a single electron and proceeding to diffraction from a thin film with multiple domains on a substrate. In order to confine the length of this discussion many of the steps in this presentation will be given without proof as many discussions of this have been given elsewhere [1-5].
2.2 CRYSTAL LATTICE STRUCTURE

Crystals are by definition, composed of identical arrangements of atoms, known as unit cells, which are repeated periodically throughout the material. The set of vectors which describe the displacement to the atoms within a unit cell from a common origin are known as the basis. In 3 dimensional space these unit cells can be viewed as parallelepipeds packed together so that the system will be unchanged when it undergoes a translation through and along the length of one of the edges of the cells and all of the space in the system is filled by the cells. The edges of these parallelepipeds can be described by vectors which are known as lattice vectors and conventionally take the form \( \mathbf{a}_1, \mathbf{a}_2, \) and \( \mathbf{a}_3 \). A unit cell which defines a given crystal lattice is not unique and can take on an infinite number of forms. The smallest possible unit cells for a given crystal are known as primitive cells. Sometimes however it may be convenient to use a larger cell with greater symmetry such cells are known as conventional unit cells.

The displacement from one unit cell in a crystal to any other can be defined by a vector composed of a linear combination of the lattice vectors of the crystal. The direction in which this displacement points is conventionally denoted by the coefficients of the lattice vectors, known as Miller Indices, surrounded by square brackets, for example \([100]\) corresponds to the direction of the vector \( \mathbf{a}_1 \) and \([111]\) corresponds to \( \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3 \). When the symmetry of a crystal is such that multiple directions are equivalent, then the set of equivalent directions is denoted by angled brackets surrounding the indices. Crystals can be divided an infinite
number of ways into planes of atoms these planes are represented by indices of the form \((hkl)\) where the direction \([hkl]\) is perpendicular to the planes. Symmetrically equivalent groups of planes are written \(\{hkl\}\).

The systems which are relevant to this thesis are Ag, Pb, Si, In and Sapphire and so only the detailed crystal structure of these materials will be discussed here. Both Ag and Pb have a face-centered-cubic structure (fcc), Si has a diamond structure which is an fcc lattice with a basis, In has a body-centered-tetragonal (bct) lattice structure and sapphire has a hexagonal structure.

The conventional unit cell of an fcc lattice is a cube and can be described by placing atoms on the corners of a cube and then placing additional atoms at the center of each face of the cube as shown in Fig 2.1(a). The lattice vectors for the conventional unit cell where the cube has sides of length \(a\) can be written.

\[
a_1 = a\hat{x}, \quad a_2 = a\hat{y}, \quad a_3 = a\hat{z}
\]

And its basis will be made up of a set of vectors

\[
0, \quad \frac{1}{2}(a_2 + a_3), \quad \frac{1}{2}(a_3 + a_1), \quad \frac{1}{2}(a_1 + a_2)
\]

A set of primitive vectors for such a lattice is

\[
a'_1 = \frac{1}{2}(a_2 + a_3), \quad a'_2 = \frac{1}{2}(a_3 + a_1), \quad a'_3 = \frac{1}{2}(a_1 + a_2)
\]

these can also be seen in Fig. 2.1(a). The diamond structure is shown in Fig. 2.1(b) which is simply the fcc lattice with an extra atom located at a displacement

\[
d = \frac{1}{4}(a_1 + a_2 + a_3)
\]

from each lattice cite in the fcc lattice.
The structure of the sapphire lattice known as the corundum structure has oxygen atoms arranged in a hexagonal close packed structure with aluminum atoms filling $\frac{2}{3}$ of the sites between each layer of oxygen. The cell of hexagonal close packed structure is shown in Fig. 2.1(c) its lattice vectors can be written

$$a_1 = a \left( \frac{\sqrt{3}}{2} \hat{x} - \frac{1}{2} \hat{y} \right), \quad a_2 = a \hat{y}, \quad a_3 = \sqrt{3} a \hat{z}$$

(2.5)

and it’s basis

$$0, \quad \frac{1}{3}(2a_1 + a_2) + \frac{1}{2} a_3$$

(2.6)

For the work done on this system here only the arrangement of atoms in the $\hat{z}$ direction is necessary and the detailed structure of the sapphire lattice is quite complicated so a complete description will not be given here. In the $\hat{z}$ direction the hexagonal unit cell of sapphire is made up of 6 equally spaced layers each with 2 Al atoms and 3 O atoms with various in-plane arrangements. If the first Al atom in the unit cell has a displacement of 0 in the $\hat{z}$ direction from the bottom of the cell and the next Al atom has a displacement of $0.4937\text{Å}$ then the 3 O atoms will be displaced by $0.8445\text{Å}$ from the bottom of the unit cell. This is repeated for the six layers in the unit cell in the $\hat{z}$ direction.

The conventional cell for a bcct lattice is shown in Fig. 2.1(d) which is a tetragon with an atom at the center. Its lattice vectors can be written

$$a_1 = a \hat{x}, \quad a_2 = a \hat{y}, \quad a_3 = c \hat{z}$$

(2.7)

and it’s basis

$$0, \quad \frac{1}{2}(a_1 + a_2 + a_3)$$

(2.8)
In the case of In it is worth noting that $a = 3.23\text{Å}$ and $c = 4.94\text{Å}$ the distance from the origin to (110) then is $4.57\text{Å}$ which is approximately $c$. The In lattice then has a structure that is almost fcc. A diagram of the unit cell that is approximately fcc is highlighted in red amongst four conventional bct unit cells in Fig. 2.2.
**Figure 2.1:** (a) The fcc conventional unit cell, the conventional lattice vectors are shown in red, lattice vectors for the primitive cell are shown in green. (b) The diamond lattice consists of a fcc lattice with an atom placed at a displacement \( \mathbf{d} \) from each atom in the fcc unit cell. (c) The hexagonal lattice, the conventional lattice vectors are shown in red, the basis vector is shown in green. (d) The bct lattice, the conventional lattice vectors are shown in red, the basis vector is shown in green.
2.3 SURFACES

When dealing with the physics of crystal systems it is often convenient and a good approximation to pretend that the crystal symmetry continues indefinitely. However in real crystals, the symmetry is always broken somewhere by the surface of the crystal. In some cases the surface can dominate certain properties of the system causing intriguing effects and so the study of surfaces has
become increasingly prominent in the study of condensed matter systems. In this section the structure of the surfaces of crystals relevant to this study will be discussed.

As discussed in the section above a crystal can be divided into planes of atoms in an infinite number of ways. A surface which truncates a crystal in a certain direction can be described by one of these planes. When discussing surfaces it may be convenient to use a unit cell, other than the conventional unit cell, so that two of the lattice vectors are in the plane of the surface. The planes which will be discussed are the \((001)\) plane of the hexagonal close packed lattice for sapphire and the \((111)\) plane on the fcc and the diamond lattice.

In the case of sapphire the surface is already parallel to two of the lattice vectors in the conventional unit cell and perpendicular to the other. Therefore in this case the conventional unit cell will be the surface unit cell.

A figure showing the conventional unit cell of an fcc lattice with a \((111)\) plane cutting through it is shown below in Fig.2.3. A lattice vector that is perpendicular to the surface will be given by

$$a'_3 = a_1 + a_2 + a_3$$

in terms of the conventional bases vectors. Two vectors perpendicular to this vector and thus parallel to the surface plane will be

$$a'_1 = \frac{1}{2}(a_1 - a_2), \quad a'_2 = \frac{1}{2}(a_2 - a_3)$$

It can be seen that these planes are also made up of a triangular mesh. These planes also do not stack directly on top of one another but are each offset from the
layer below so that every third layer will line up with the original layer. This layering can therefore be said to have an ABCABC stacking. This structure is shown in Fig. 2.4.

**Figure 2.3:** Conventional fcc unit cell with \((111)\) planes running through it.
The diamond lattice is the same as the fcc lattice except that there is an extra atom at a displacement, given by \( \frac{1}{3} \mathbf{a}_j' \), from each atom in the fcc lattice. The basis for a diamond lattice will then be

\[
\mathbf{v}, \quad \frac{1}{3}(2\mathbf{a}_1' + \mathbf{a}_2') + \frac{1}{3} \mathbf{a}_3' + \mathbf{v}, \quad \frac{1}{3}(2\mathbf{a}_1' + \mathbf{a}_2') + \frac{2}{3} \mathbf{a}_3' + \mathbf{v}
\]

(2.11)

where \( \mathbf{v} \) can take the values \( \mathbf{v} = 0 \) or \( \mathbf{v} = \frac{1}{3} \mathbf{a}_j' \). A cross section of the diamond lattice is shown in Fig. 2.5. The diamond lattice, as in the case of an fcc lattice, has three sets of layers, however here the single layers are replaced by bilayers.
separated by $\frac{1}{12}a'\alpha$. There are two distinct positions at which this surface can be truncated, between the bilayers or within a bilayer. X-ray reflectivity experiments have shown that the Si surface is truncated between the bilayers [6]. It will therefore be more convenient to modify the basis in Eq. 2.11 so that

$$v = 0 \quad \text{or} \quad v = -\frac{1}{12}a'\alpha$$

so that the unit cell will be truncated appropriately.

\[\text{Figure 2.5: Cross section of a diamond lattice terminated by a (111) plane}\]

When a surface is truncated the atoms in the planes near the surface generally do not have the same structure as those in the bulk. The atoms in the
plane at the surface have no atoms above them to bond with, in the way that the atoms in the bulk do. Dangling bonds would therefore be present if the surface was terminated with a bulk like plane. These atoms and those just below them therefore are likely to find it energetically favorable to rearrange into a new planar structure in order to lower their energy by creating new bonds. Such a rearrangement is known as a surface reconstruction. Other material can be absorbed on the surface causing further reconstructions.

To describe a surface reconstruction, typically the periodicity of the surface atoms is given using a convention known as Wood’s notation. This system gives the periodicity of the reconstruction in terms of the bulk surface lattice constants. If we consider a crystal with a chemical formula A terminated in the \([h \ k \ l]\) direction and having surface lattice vectors \(a_1\) and \(a_2\), and a surface reconstruction that has a cell with vectors \(r_1\) and \(r_2\) so that \(r_i = n_i a_i\) then the reconstruction will be described by \(A(hkl)-(n_1 \times n_2)\). If the vectors describing the reconstruction are rotated from the surface lattice vectors by an angle \(\phi\) then the notation describing the reconstruction will be \(A(hkl)-(n_1 \times n_2)R\phi\) and if the reconstruction is brought about by an absorbant B the notation will be \(A(hkl)-(n_1 \times n_2)R\phi-B\). Upon burial by a thin film the surface interface may change dramatically. The reconstruction could even be completely removed leaving the substrate in the bulk termination.

In an ideal situation during thin film growth the material deposited will form a single layer at a time, not beginning a new layer until the one beneath it is
complete. In reality this is rarely the case, and domains with different thicknesses will be present. Islands separated by areas where there is nothing on the surface may also be present. To further complicate matters the distances between layers in a film are likely to relax. These modulations in the layer spacing will be dependent on the thickness of the film.

2.4 THEORY OF DIFFRACTION

Consider a plane wave propagating in the $\hat{z}$ direction and polarized in the $\hat{\epsilon}$ direction with an electric field

$$E = E_0 e^{i(kz - \omega t)} \hat{\epsilon}$$

(2.13)

incident upon an electron. Here $k$ defines the frequency in space and $\omega$ the frequency in time. The electric field will apply a force to the electron resulting in an oscillation of the electron, where its acceleration is given by

$$a(t) = \frac{F(t)}{m_e} = \frac{eE_0}{m_e} e^{-i\omega t} \hat{z}$$

(2.14)

This oscillating electron will give rise to another field. The amplitude of the scattered radiation resulting from light with an initial momentum $\mathbf{k}_i$ scattering from an electron at some displacement $\mathbf{r}$ from the origin that is observed along the direction of a scattered wave with momentum $\mathbf{k}_f$ is given by

$$A(\mathbf{r}, t) = A_0 \frac{e^2}{4\pi\varepsilon_0 m_e c^2 R_0} e^{-i(k_f - k_i) \cdot \mathbf{r}}$$

(2.15)
where $A_0$ is the amplitude of the incident wave and $R_0$ is the distance between the particle and the observer and results from the spherical nature of the scattered wave. The scattering cross section of an electron is given by the Thompson formula

$$\frac{d\sigma}{d\Omega} = P r_0^2$$

(2.16)

$$r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} = 1.617 \times 10^{-5} \text{ Å}$$

(2.17)

where $P$ is a polarization factor and the term $r_0$ is the Thompson scattering length. Light can also be scattered by protons in the nucleus of an atom however the mass of the nucleus will be much larger and its scattering cross section much smaller than that of the electrons. The scattering resulting from the nucleus therefore is negligible. To calculate the amplitude of light scattered from a group of particles the scattering amplitudes from each particle must be summed together and the square modulus of this sum of amplitudes must be taken to get the intensity. To get the amplitude of light scattered from an atom the amplitudes from all the electrons in the atom must be summed together. Due to the quantum mechanical nature of electrons in an atom, instead of summing the amplitude at each electron position the density of electrons $\rho(r)$ is integrated over all space around the atom

$$A_{\text{atom}}(q) = \frac{A_0 r_0}{R_0} \int \rho(r) e^{iqr} d^3 r$$

(2.18)

where $q = k_f - k_i$. The electron density will be defined by the wave function of the electrons in the atom. The part of this equation in the integral
is known as the atomic scattering factor. The atomic scattering factors for almost all elements have been determined and can be looked up in a table [7]. To calculate the scattering amplitude of light scattered from the unit cell of a crystal the amplitudes contributed from each atom must be summed

\[ A_{\text{cell}}(q) = \frac{A_i r_0}{R_0} \sum_{j \text{cell}} f(q) e^{i q \cdot R_j} \]  \hspace{1cm} (2.20)

where \( R_j \) is the position of the \( j \)th atom in the unit cell. The summation

\[ F(q) = \sum_{j \text{cell}} f(q) e^{i q \cdot R_j} \]  \hspace{1cm} (2.21)

is generally known as the structure factor. Finally the amplitudes resulting from all the unit cells in the lattice must be considered. For a crystal with lattice constants \( a_1 \), \( a_2 \) and \( a_3 \) the scattering amplitude can be written

\[ A_{\text{crystal}} = \frac{A_i r_0}{R_0} F(q) S_{N_1}(q \cdot a_1) S_{N_2}(q \cdot a_2) S_{N_3}(q \cdot a_3) \]  \hspace{1cm} (2.22)

where the crystal extends \( N_j \) unit cells in the direction of \( a_j \). The term \( S_{N}(q \cdot a) \) can be written

\[ S_{N}(q \cdot a) = \sum_{n=0}^{N-1} e^{i q n a} = \frac{1 - e^{i Nq a}}{1 - e^{i q a}} \]  \hspace{1cm} (2.23)

and its square modulus will be

\[ |S_{N}(q \cdot a)|^2 = \frac{\sin^2 \left( \frac{1}{2} Nq \cdot a \right)}{\sin^2 \left( \frac{1}{2} q \cdot a \right)} \]  \hspace{1cm} (2.24)
a function that is known as the N slit interference function. The intensity of light scattered from the crystal will be

\[ I_{\text{crystal}} = \left( \frac{A_0}{R_0} \right)^2 |F(q)|^2 |S_{N_1}(q \cdot a)|^2 |S_{N_2}(q \cdot a_2)|^2 |S_{N_3}(q \cdot a_3)|^2 \] (2.25)

This equation assumes that the atoms in the lattice are stationary and do not move. The atoms in any lattice will vibrate around their equilibrium positions however and this must be taken into account. This can be done by multiplying the right side of Eq. 2.25 by the Debye Waller factor \( e^{-M} \), where \( M = \frac{1}{2} q^2 \left< u_q^2 \right> \) and \( \left< u_q^2 \right> \) is the magnitude of the average displacement squared of the atom from its equilibrium position in the \( q \) direction. This term will lower the intensity as the temperature is increased and will also cause the intensity to decrease as a function of the momentum transfer. The amplitude of the vibrations will not necessarily be isotropic and can introduce peaks in the scattering intensity known as thermal diffuse scattering along high symmetry directions. These features are quite weak and broad compared to the features resulting from the equilibrium structure and can simply be assumed to be part of the background which will be subtracted out.

For a bulk crystal, \( N \) will be very large and \( |S_{N}(q \cdot a)|^2 \) will take the value \( N^2 \) when \( q \cdot a = 2\pi n \), where \( n \) is an integer, and otherwise will be near zero. There will then be a lattice of points in the space of the momentum transfer, commonly known as reciprocal space, where the intensity will be peaked. These peaks in intensity are known as Bragg peaks. The reciprocal space lattice will be spanned by a basis made up of three vectors \( b_j \) defined by
\[ \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (2.26) \]

where \( \mathbf{a}_i \) is a real space lattice vector. These vectors will then take the form

\[ \mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (2.27) \]

\[ \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (2.28) \]

\[ \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (2.29) \]

and any lattice point in reciprocal space may be written

\[ \mathbf{q} = H\mathbf{b}_1 + K\mathbf{b}_2 + L\mathbf{b}_3 \quad (2.30) \]

where \( H, K \) and \( L \) are integers.

In many types of experiments one may be able to view a wide range of the directions of the outgoing momentum of scattered radiation for a given incident momentum. The points in reciprocal space that can be observed are given by \( \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \) and can then be determined by considering all the possible values of \( \mathbf{k}_f \). Since we are considering only elastic scattering the magnitude of \( \mathbf{k}_f \) is fixed so that \( |\mathbf{k}_f| = |\mathbf{k}_i| \) and the points in reciprocal space which can be observed will make up a sphere centered at a point in reciprocal space \(-\mathbf{k}_i\) from the origin. This sphere is known as an Ewald sphere, an example of an Ewald sphere in a cross section of reciprocal space is shown in Fig. 2.6.
Figure 2.6: A cross section of an Ewald sphere in reciprocal space. The sphere is centered at a displacement $\mathbf{k}_i$ from the origin in reciprocal space. Any points in reciprocal space along the perimeter of the sphere can be observed for a given $\mathbf{k}_i$.

2.5 EXPERIMENTAL CORRECTIONS

2.5.1 Polarization Factor

The intensities as calculated so far are still subject to a number of corrections related to the geometry of the experiment [8]. The first is a result of
the polarization of the incoming beam as compared to the outgoing beam. The true intensity must be multiplied by a polarization factor $|\boldsymbol{\varepsilon}_i \cdot \boldsymbol{\varepsilon}_f|$ where $\boldsymbol{\varepsilon}_i$ is the polarization vector of the incident x-ray beam and $\boldsymbol{\varepsilon}_f$ that of the scattered x-rays.

A synchrotron source was used to generate x-rays for this experiment the electrons which are used to generate x-rays here are accelerated in the horizontal plane resulting in an incident beam with a polarization in the horizontal direction. The goniometer used in this work holds the sample so that if the angle between the incident beam and the sample surface is set to zero $\boldsymbol{\varepsilon}_i$ will be perpendicular to the surface. The polarization factor will be given by

$$C_p = 1 - \left( \sin(\mu) \cos(\gamma) \cos(\delta) + \cos(\mu) \sin(\gamma) \right)^2$$

(2.31)

In the case of the reflectivity $\delta = 0$ and $\mu = \gamma$ so the polarization can be reduced to

$$C_p = 1 - \left( \sin(\mu) \cos(\mu) + \cos(\mu) \sin(\mu) \right)^2 = \cos^2(2\mu)$$

(2.32)

in this situation.

### 2.5.2 Lorentz Factor

The equation for intensity given in Eq. 2.25 is given in terms of the coordinates in reciprocal space. The detector however is integrating the intensity over an area in real space or angular space. A transformation is therefore needed to convert the calculated intensity from reciprocal space to angular space. This can be done by taking the inverse of the Jacobian which transforms the coordinate system from angular space to reciprocal space. For the reflectivity this correction will be
\[ C_L = \frac{1}{\sin(\mu)} \]  

(2.33)

2.5.3 Beam Footprint

Only the portion of the sample surface that is illuminated by the incident x-ray beam will contribute to the measured intensity at a given scattering angle. If an incoming beam has a cross-sectional area \( A \) then the area on the surface that is illuminated by the incident beam will be \( A' = A / \sin(\mu) \) where \( \mu \) is the angle between the incident beam and the sample surface. The calculated intensity will therefore need to be multiplied by a factor of

\[ C_A = \frac{1}{\sin(\mu)} \]  

(2.34)

If however the angle of the incident beam is such that the entire width of the sample is exposed to the beam

\[ C_A = \frac{s_w}{b_w} \]  

(2.35)

where \( s_w \) is the width of the sample and \( b_w \) is the width of the beam.

2.6 DIFFRACTION FROM A THIN FILM

A thin film or a surface reconstruction will be bulk like in two dimensions but will only be several layers thick in the other direction. If surface lattice vectors are chosen to describe the lattice coordinates such that \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are in the plane of the surface but \( \mathbf{a}_3 \) is perpendicular to the surface, then the first two
\[ |S_N(q \cdot a)|^2 \] terms in Eq. 2.25 will behave like Dirac delta functions but the third will not. The intensity will peak when the in-plane components of the momentum transfer are at reciprocal lattice sites

\[ \mathbf{q}_i = H\mathbf{b}_1 + K\mathbf{b}_2 \]  

(2.36)

where H and K are integers, however it will not be strongly peaked along the out of plane component. The intensity will therefore exist in rods in reciprocal space as shown in Fig. 2.7. These rods are known as crystal truncation rods [9]. For a thin film, ignoring the structure factor, the intensity as a function of the out of plane momentum transfer along a rod will take the form of \[ |S_N(q \cdot a_3)|^2 \]. Here \( a_3 \) is again chosen to be perpendicular to the surface. A plot of \[ |S_7(2\pi x)|^2 \] is shown in Fig. 2.8, giving a rough idea of what the intensity along a rod of a 7 layer film would look like. The function is periodic repeating every integer, which corresponds to every Bragg peak in a bulk lattice. There are peaks at the integer values that rise to \( N^2 \) and 5 or \( N-2 \) fringes between these peaks. The dominant thickness in a thin film can be deduced from a CTR by counting the number of fringes between the Bragg peaks and adding two.
**Figure 2.7:** Cartoon illustrating crystal truncation rods, the surface reciprocal lattice is shown in gray at the bottom the red spheres represent bulk like peaks in reciprocal space and the crystal truncation rods are blue.
Figure 2.8: (a) The function $|S_7(2\pi x)|^2$ plotted as a function of $x$ and (b) its logarithm.

In reality films are not free standing and exist on a substrate which must be taken into consideration when trying to model the intensity observed in an experiment. Furthermore as discussed in section 2.3 the structure of a film is generally not as simple as in the argument above so that relaxations and domains of differing thicknesses must be accounted for.
To get the structure factor of the substrate Eq. 2.21 can be used. If a surface coordinate system, where \( a_1 \) and \( a_2 \) are in the plane of the surface, is used then the first two summations will be unchanged and the third will go from 0 to negative infinity. In this work the only data that was analyzed that involved a significant contribution, to the intensity, from the substrate was the reflectivity data. The reflectivity data only involves the intensity where the in-plane components of the momentum transfer are zero. The momentum transfer can therefore be written \( q = Lb_3 \). The part of the scattering amplitude in terms of \( L \) that were needed to calculate the relative intensities along such a scan is then

\[
A_{\text{sub}}(L) \propto F_{\text{sub}}(L) \sum_{n=0}^{\infty} e^{-2\pi n L - n a_{\text{att}}} = F_{\text{sub}}(L) \frac{1}{1-e^{-2\pi n L - n a_{\text{att}}}} \quad (2.37)
\]

where \( a_{\text{att}} \) is an attenuation factor, so that the intensity of the beam diminishes by a factor of \( e^{a_{\text{att}}} \) for every layer it passes through. The attenuation will be small and will not have a significant effect on the final equation except at the Bragg peak position and can be taken as 0 for our purposes.

The surface of the substrate could be somewhat rough. A model which is frequently used to simulate roughness on a substrate assumes that the first layer above the last completely occupied layer of material occupies a fraction \( \beta \) of the surface. The next layer is assumed to occupy the same fraction of the layer just below it so that it occupies a fraction \( \beta^2 \) of the total surface. Continuing in this manner the \( n \)th layer above the last complete layer will occupy a fraction \( \beta^n \) of the total surface. This introduces a correction factor
\[ I_{\text{rough}} = I_{\text{ideal}} \frac{(1-\beta)^2}{1 + \beta^2 - 2\beta \cos(a_3 \cdot q)} \]  

(2.38)

to the measured intensity [12]. For the substrates used in these experiments it was found that the roughness of the substrate did not have a significant effect on the intensity.

The substrates to be discussed are the Si(111) and the Sapphire(001) substrate.

The structure factor for a Si(111) substrate can be calculated using the coordinates of the basis found in Eq. 2.11

\[
F_{\text{Si}}(L) = f_{\text{Si}}(L)e^{-M_{\text{Si}}} \left( 1 + e^{\frac{2\pi nl}{12}} \right) \left( 1 + e^{\frac{2\pi nl}{3}} + e^{\frac{4\pi nl}{3}} \right)
\]  

(2.39)

where \( f_{\text{Si}}(L) \) is the atomic scattering factor for Si and \( M_{\text{Si}} \) is the Debye Waller factor. The scattering amplitude can therefore be written

\[
A_{\text{Si}}(L) \propto f_{\text{Si}}(L)e^{-M_{\text{Si}}} \frac{1 + e^{\frac{2\pi nl}{12}}}{1 - e^{\frac{2\pi nl}{3}}}
\]  

(2.40)

The structure factor for the sapphire substrate can be calculated using the coordinates discussed in section 2.2.

\[
F_{\text{Sapp}}(L) = \left( f_{\text{Al}}(L)e^{-M_{\text{Al}}} \left( 1 + e^{2\pi i0.038L} \right) + 3f_{\text{O}}(L)e^{-M_{\text{O}}}e^{2\pi i0.065L} \right)
\]  

(2.41)

The scattering amplitude for this substrate can be written

\[
A_{\text{Sapp}}(L) \propto \frac{F_{\text{Sapp}}(L)}{1 - e^{\frac{2\pi nl}{6}}}
\]  

(2.42)
To calculate a thin film's contribution to the scattering amplitude, lattice relaxations and domain sizes with varying thicknesses must be taken into consideration. This scattering amplitude for a film with only one type of atom can be written

\[
A_{\text{film}}(q) \propto F_{\text{film}}(q) \frac{1}{1 - e^{iqa_1}} \frac{1}{1 - e^{iqa_2}} \sum_{j=1}^{N} p_N \sum_{j=1}^{N} e^{iqa_{j,N}}
\]

(2.43)

where \( N \) is the film thickness, \( p_N \) is the fraction of the surface area covered by a film of thickness \( N \), \( q_\perp \) is the component of the momentum transfer perpendicular to the sample surface and \( z_{j,N} \) is the distance between the \( j-1 \)th and the \( j \)th layer. The first summation is over all possible thicknesses present in the thin film [6].

Now that the scattering amplitudes for a general thin film and specifically for the substrates of interest in this study have been given, the intensity can be calculated. If the different domains that exist on the substrate all contribute to the intensity coherently the intensity will simply be

\[
I_{\text{coh}} = |A_{\text{film}} + A_{\text{sub}}|^2
\]

(2.44)

Some of the distances between domains in the film however will be greater than the coherence length of the x-rays and needed to be summed together incoherently. To take this into account another term will be needed where the intensities from different film thicknesses are summed incoherently. This term will take the form

\[
I_{\text{incoh}}(q) = \sum_{N>0} p_N \left| F_{\text{film}}(q) \frac{1}{1 - e^{iqa_1}} \frac{1}{1 - e^{iqa_2}} \sum_{j=1}^{N} e^{iqa_{j,N}} + A_{\text{sub}}(q) \right|^2 \]

\[ + p_0 \left| A_{\text{sub}}(q) \right|^2 \]

(2.45)
here the scattering amplitude for a given thickness is added coherently with the amplitude of the substrate the intensities from each thickness times the fraction of the surface covered by that thickness is then summed over all thicknesses. The total intensity can then be taken by adding the coherent and incoherent parts of the intensity together using a coherence factor $\Lambda$

$$I = \Lambda I_{\text{coh}} + (1 - \Lambda)I_{\text{incoh}}$$  \hspace{1cm} (2.46)

By making the appropriate corrections this equation can be used to fit experimentally acquired x-ray data.

REFERENCES


CHAPTER 3

EXPERIMENTAL METHODS

3.1 INTRODUCTION

This section will provide a brief overview of the experimental techniques and equipment used to carry out this research.

The primary technique used is x-ray diffraction from a synchrotron source. There are \( \sim 10^9 \) times as many scatterers in a surface layer as there are in the bulk of a sample which often makes it impractical to use a laboratory source to conduct surface x-ray diffraction experiments. Synchrotron sources however can produce photon intensities \( \sim 10^{10} \) times greater than a laboratory source and therefore make surface diffraction experiments that would otherwise be impractical, routine. All of the x-rays used in this study were generated using an undulator beam line. The station where the experiments were carried out (Hutch 33-ID-E) contains a UHV chamber mounted on a diffractometer. There are many methods used to detect x-rays but the ones used for the experimental work described here are ion chambers, scintillation detectors, and CCD detectors.

For the thin film experiments done in this work it is of great importance that the samples be kept free of any contaminants that would alter their chemical makeup and structure. An ultrahigh vacuum (UHV) environment \( (\sim 10^{-10} \text{Torr}) \) is therefore necessary to carry out these experiments and so the technology used to
create such an environment will be discussed. A more thorough discussion of UHV technology and techniques can be found in the following references [1, 2].

Before and during the use of limited beamtime at a synchrotron source preparing the sample surface, depositing thin films and characterizing the surface is vital to a successful experiment. The techniques that were used for preparation and characterization will thus be addressed.

The final section of this chapter will explain the techniques used to collect and process the x-ray intensity data. In this work reflectivity and reciprocal space maps were collected.

### 3.2 SYNCHROTRON RADIATION

#### 3.2.1 Synchrotron Sources

Improvements in x-ray sources have been dramatic since Roentgen first characterized x-rays in 1895. Eventually it was found that electron storage rings used in high energy experiments could be used to generate x-ray beams with much greater brilliance than other available sources. This discovery has led to the development of synchrotron sources dedicated to generating x-rays, thus opening up entire fields of science to x-ray based techniques that would otherwise be impractical or impossible.

A synchrotron is a type of particle accelerator which accelerates charged particles through a narrow approximately circular path maintained at ultrahigh vacuum pressures. In these accelerators an injection system makes the particles
available to the synchrotron in bunches. Bending magnets modify the path of the particle bunches to keep them moving in the appropriate trajectory and a high-frequency electric field accelerates them tangentially. As the particle bunches are circulated the magnetic and electric fields are modified so that they continue to move along the appropriate path. As implied above the trajectory of the particle beam is not necessarily circular and generally consists of long straight sections terminated by bending sections where the bending magnets reside.

When discussing synchrotron radiation the particles involved in generating the radiation are generally electrons. Anytime a force acts on a charged particle causing it to accelerate or change directions radiation is given off. There are a few ways in which synchrotron radiation are typically generated from a synchrotron. When the path of the beam is bent by the bending magnets synchrotron radiation is generated. Synchrotron radiation can also be generated by passing the particle beam through an insertion device such as a wiggler or an undulator. The x-rays used in the experiments presented in this thesis were generated using synchrotron radiation from the Advanced Photon Source (APS) using the undulator source at sector 33.
3.2.2 Undulators and Beamline Optics

Synchrotron radiation is emitted when the electron beam in the synchrotron passes through a magnetic field. Many beamlines simply use the radiation generated when the electron beam passes through the bending magnets in the synchrotron. X-ray beams of much greater intensity however, can be generated by passing the electron beam through an insertion device known as a wiggler or an undulator. These devices are made up of alternating magnetic dipoles and can be placed in the straight sections of a synchrotron. Passing the electron beam through one of these devices causes it to accelerate in a sinusoidal
trajectory resulting in the generation of radiation. An illustration of such a device and the trajectory of a particle passing through it are shown in Fig. 3.2.

For an insertion device with \( N \) such dipoles \( N \) times as much radiation can be generated as could be with a single magnet. When an electron moves in a sinusoidal trajectory, the magnitude of its acceleration is greatest at the top and bottom of the oscillations. The majority of the synchrotron radiation is therefore emitted at these points. By carefully controlling the trajectory and therefore the period at which the electrons oscillate one can insure that a certain fundamental frequency of the radiation spectrum and its harmonics add coherently. Undulators are distinct from wigglers in that they make use of this controlling the strength of the magnetic field by controlling the distance between the magnetic dipoles, denoted by \( d \) in Fig. 3.2. This effectively concentrates the energy spectrum of the radiation to a narrow range of frequencies.
Figure 3.2: A schematic of an undulator. An electron beam passes between a series of dipole magnets that make up the undulator. The path of the electron beam is bent by the magnetic field that is produced by the undulator so that it follows a sinusoidal path as shown by the curved blue line.

The energy spectrum of synchrotron radiation is much too wide for many experimental techniques. Energies therefore must be selected using a monochromator. The monochromator at sector 33ID uses two Si crystals as shown in Fig. 3.3. A specific energy is selected by setting the angle between the incident beam and the Si crystal to the angle at which Bragg’s law $2d \sin \theta = n\lambda$ is
satisfied for the desired wavelength. Only the photons with the selected energy and their harmonics are then diffracted to the second crystal. The second crystal redirects the beam so that it continues along the same direction as the original incident beam. The second crystal in the monochromator at sector 33ID can be bent so that it is curved along its width. By bending the crystal in this way the beam can be focused in the horizontal direction (sagittal focusing).

Figure 3.3: A schematic of the monochromater. A white beam reflects from two nearly perfect crystals so that photons of only one energy and there harmonics pass through.

After going through the monochromator the beam still contains harmonics of the desired energy. At the beamline at sector 33ID these are removed by passing the beam through another set of two mirrors in an arrangement similar to that of the monochromator. For this set of mirrors however the angle is set much smaller, below the angle of total external reflection. The angle of total external
reflection will be smaller for higher harmonics, therefore if the angle is set smaller than the angle of total external reflection for the fundamental energy but higher than that for its first harmonic, nearly all of the photons that have the desired energy will be reflected but many of the higher energy harmonics will not be. At 33ID this system is rotated by an angle of 90° around the beam axis, with respect to the monochromator, and the first mirror of this system can be bent to focus the beam vertically.

3.3 X-RAY DETECTORS

Now that an explanation of the method through which x-rays are generated for the experiments in this thesis has been given, the detection of x-rays needs to be discussed. There are many types of systems that have been devised to detect and count x-rays. This section will be limited to the three detectors used to carry out the experiments presented in this work, the ion chamber, the scintillation detector and the charge coupled device (CCD).

3.3.1 Ion Chamber

An ion chamber consists of a cavity filled with some type of gas between two plates across which a high voltage can be applied, usually on the order of a few hundred volts. In our experiments the cavity is simply filled with air. When an x-ray passes through the cavity there is a small probability that it will collide with and ionize a gas molecule, resulting in an ion current across the plates. This ion current will be proportional to the number of x-ray photons passing through the chamber. Because this detector allows most of the photons that enter it to pass
through unimpeded it is ideal for giving a number which is proportional to the number of photons in the incident beam. Small fluctuations in the incident beam will cause similar undesirable fluctuations in the measured intensity in a diffraction experiment. Dividing the diffracted intensity by the intensity of the incident beam, measured by the ion chamber, normalizes it removing the unwanted fluctuations. Because a very high voltage is required there is often a small leakage current present, between the plates, even when there are no photons. This leakage current, results in a count rate known as the dark count that must be subtracted from the count rate observed when photons are present. The dark count can vary over time and must be measured periodically.

3.3.2 Scintillator Detector

A scintillation detector is made up of two parts a scintillating material and a photomultiplier tube. When an x-ray strikes the scintillating material it scintillates (fluoresces) giving off ultra violet light. This ultra violet light then causes the photocathode, in the photomultiplier tube, to emit electrons. These electrons give rise to a pulse in the voltage across the photomultiplier tube. These pulses are shaped and counted by appropriate electronic devices giving a number that is quite close to the actually number of x-rays incident on the surface of the detector. The height of the pulses will be roughly proportional to the energy of the x-ray photon which produced it and thus provides some energy resolution. These pulses can be measured on an oscilloscope and a range of voltages can be set so that only the photons of the desired energy are counted and photons with higher or lower energy such as those from harmonics or fluorescence are not.
This detector can count photons quite quickly however it will be unable to count photons for a very short period time $\sim \mu s$ after it begins counting a photon. This period of time is known as the dead time of a detector and gives rise to a correction in the count rate where the true count rate is given by

$$N_{true} = \frac{N_{obs}}{1 - \tau N_{obs}}$$  

(3.1)

where $N_{obs}$ is the observed count rate and $\tau$ is the dead time. The dead time for the detector used here was measured to be 0.906 $\mu s$. The true count rate maintains a relationship to the observed count rate that is quite linear up to about $10^5 \frac{\text{counts}}{s}$.

This detector is quite fast and quite sensitive so great care must be taken to avoid exposing this detector to count rates which are too high, such as when the detector is measuring a Bragg peak. A set of titanium and aluminum filters are thus used, to attenuate the direct beam, when the detector is exposed to such high count rates. The experimental count rate must then be corrected by dividing by the appropriate attenuation factor.

### 3.3.3 CCD

Both the ion chamber and the scintillation detector are not sensitive to which region on the surface of the detector was struck by a photon and are therefore known as point detectors. This is the advantage of a CCD; it is an area detector which can provide an image of the beam. The CCD uses a fluorescent surface that emits optical light when impinged upon by an x-ray. This light is connected to an array of photodiodes, which make up the pixels of the CCD,
though optical fibers. The optical light excites electron hole pairs in the photodiodes. The electrons are trapped by a positive potential and the charge collected will be proportional to the x-ray intensity. Although these devices do not calculate photons directly the charge is quite linear to the photon intensity.

3.4 THE SURFACE AND INTERFACE STATION AT SECTOR 33

The x-ray diffraction experiments described in this work all took place at the surface experimental station in the E hutch of sector 33ID at the Advanced Photon Source. This hutch houses an ultrahigh vacuum (UHV) chamber mounted on a six circle diffractometer as described in reference [3].

A diagram of this type of diffractometer is shown in Fig. 3.4. There are six angles that can be manipulated to allow a wide range of reciprocal space to be explored during x-ray diffraction experiments [4]. Because there are six degrees of angular freedom and only three dimensions in reciprocal space, there are multiple ways in which a point in reciprocal space can be reached. In the mode used here the two angles $\chi$ and $\phi$ are used to align the optical normal of the sample surface with the $\theta$ axis. The angle $\phi$ rotates the sample directly and sits in $\chi$ which tilts the $\phi$ axis and sits in $\theta$ which rotates this entire assembly. When the above restriction is imposed $\theta$ rotates the sample around its surface normal. The detector is mounted on an arm and can be moved out of the surface plane by the angle denoted by $\gamma$ this arm sits on the $\delta$ circle which allows the detector to move in the direction in the surface plane. All of these circles sit on a table that
can be rotated by the angle $\mu$ which allows the angle between the surface normal and the incident beam to be manipulated. One more restriction still must be imposed in the experiments done here the angle $\mu$ was kept equal to $\gamma$. All of the motions of the diffractometer are achieved by stepping motors which use speed-reducing gear boxes to achieve an angular resolution of approximately $0.0005^\circ$. The entire diffractometer sits on a table which can be translated vertically or horizontally perpendicular to the beam so that the center of the diffractometer can be placed in the beam. Four more motors can tilt the table to insure that it is level.

**Figure 3.4:** Schematic of the diffractometer showing all diffractometer circles, the sample and detector are labeled.
A UHV chamber sits on top of the \( \mu \) table and is connected to the \( \phi \) circle through a differential stage which is pumped by an ion pump. This chamber is equipped with a number of standard tools used to conduct surface science experiments. A picture of this system is shown in Fig. 3.5 and many of the components are labeled. The system is pumped by a sputtering ion pump and a titanium sublimation pump (TSP) and has a base pressure below \( 10^{-10} \) torr. A turbo pump can be attached to the system for rough pumping. Two ports are available for evaporators and MBE and e-beam evaporators can be used. The evaporation rate can be determined by a crystal thickness monitor, which can be placed in the position of the sample. A reflection high energy electron diffraction (RHEED) system allows for surface characterization during preparation and can be used when x-rays are not available. When conducting x-ray diffraction experiments the sample sits behind a beryllium window in the shape of a 6” diameter semi cylinder. Beryllium is a low Z material and so allows x-rays to enter and exit the chamber without attenuating them significantly. The sample is mounted on a sample arm. The sample arm is attached to the UHV system by a long flexible bellow which can be compressed to place the sample in the path of the RHEED system or expanded for placement in the path of the x-ray beam. The sample arm contains a line through which liquid nitrogen can flow to cool the sample mount. A picture of the sample holder assembly is shown in Fig. 3.6. A sapphire block thermally anchors the sample to the sample arm while keeping it electrically isolated. The sample is mounted by two tantalum clips also act as electrical contacts allowing current to be flowed directly through the sample and
heat it through resistive heating. The end of a thermocouple is in contact with each tantalum clip to measure the temperature of the sample. A tungsten filament is mounted behind the sample. By running current through this filament the sample can be heated indirectly, high voltage can then be applied between the sample and the filament causing electrons to bombard the back of the sample heating it further.
Figure 3.5: The UHV chamber at sector 33 with many of its components labeled.
Figure 3.6: Picture of the sample holder reproduced from reference [3].

3.5 ULTRA HIGH VACUUM

3.5.1 Necessity of UHV

Any exposed surface will be impinged upon by the gas molecules that exist in its ambient environment. When conducting experiments in which the atomic scale properties of a surface are of interest, these molecules can stick to the surface causing undesirable effects. Therefore to conduct such surface science experiments the amount of gas molecules that are present in the environment of
the sample must be limited so that they do not have a significant effect on the sample.

To carry out surface experiments the time required for a significant number of molecules to stick to the surface needs to be longer than the time needed to carry out the experiment. The rate at which gas molecules will arrive on a surface from the gas phase is given by the kinetic formula [2]

\[ R = \frac{P}{\sqrt{2\pi mk_b T}} \]  

(3.2)

\( P \) is the pressure \( m \) is the molecular mass \( k_b \) is Boltzmann’s constant and \( T \) is the temperature. The average time for a gas molecule to impinge upon a surface atom is then

\[ \tau = \frac{N}{S_c R} \]  

(3.3)

where \( N \) is the number of atoms on the surface per unit area. The term \( S_c \) denotes the sticking coefficient it can vary between 1, in which every gas molecule which contacts the surface sticks and 0, in which none of them stick. The surface density for most materials is on the order of \( 10^{19} \text{ atoms/m}^2 \) and the molecular mass for a typical contaminant in a vacuum system is on the order of \( 10^{-28} \text{ kg} \). For a system at room temperature and \( P = 10^{-6} \text{ Torr} \) and assuming \( S_c = 1 \) a worst case scenario the time required to saturate the surface would be approximately \( 1 s \) a time much too short to carry out the experiments involved in this work. The pressure required to make this time several hours will be on the order of \( 10^{-10} \text{ Torr} \) a pressure range commonly known as ultrahigh vacuum (UHV).
3.5.2 Obtaining and Measuring UHV Pressures

To obtain UHV pressures a chamber must be built from appropriate materials. The chamber must be able to keep out contaminants from outside. Materials used to make the chamber and to be put inside of it must not desorb an excessive amount of unwanted contaminants into the system. UHV chambers are typically made out of stainless steel, glass or aluminum. A chamber made primarily from stainless steel was used for the experiments described in this thesis. Stainless steel has its own advantages and disadvantages. It is modular and isn’t easily broken like glass, and it is mechanically stronger than aluminum, however it tends to contain a great deal of hydrogen which can diffuse to the surface and limit the ultimate pressure of the system. In order to conduct complex experiments many components are needed in the chamber and these pieces are fitted together using flanges in which a copper gasket is set between knife edges which dig into the gasket sealing the inside of the chamber from the atmosphere. Great care must be taken to ensure all of the parts to be put inside of the chamber are clean and free of grease and oils. Surgical gloves must be used to handle UHV components to keep them free from the oils that exist on a researcher's hands. Components placed in the system must be cleaned using processes such as acid etching or sonication in a bath of organic solvents. Tools used to handle UHV components must also be degreased.

Pumping out a chamber from atmospheric to UHV pressures cannot be done by a single pump but must be done in stages by a series of pumps. The pumps used in this work are a mechanical roughing pump, a turbomolecular (or
turbo) pump, an ion pump and a titanium sublimation pump. Each of these pumps has a limited range of pressures in which it can work and a minimum pressure which can be achieved by its use.

When the chamber is pumped down from atmospheric pressure a turbo pump backed by a mechanical roughing pump is used. The turbo pump uses a series of turbines which spin at high speed (10,000 to 100,000 rpm). These turbines collide with gas molecules imparting momentum to them in a preferential direction, toward the pumps outlet. To achieve these high speeds these pumps operate in the molecular flow regime, therefore the outlet of the pump must be maintained at low pressure by some type of roughing pump. This pump, a rotary vane pump in our case, keeps the outlet of the turbo pump at rough pressure of $\sim 10^{-3}$ Torr. The lowest pressure which can be attained by the turbo pump in our setup is typically on the order of $\sim 10^{-7}$ Torr and it cannot achieve the pressures needed in this work; therefore when the pressure is at $\sim 10^{-5}$ Torr or lower a sputtering ion pump is used to attain even lower pressures.

The working part of a sputter ion pump is made up of hollow cylindrical anodes arranged lengthwise between titanium and tantalum plates that act as a cathode. A high voltage of several kV is placed between the anodes and cathodes causing the emission of electrons from the cathode surface. A magnetic field applied along the axis of the anodes causes the electrons to move in a spiral pattern increasing the chances that they will collide with and ionize gas molecules that are present in the system. These ionized molecules then collide with the cathodes where they are buried or interact with the Ti and Ta to form solid
material. The collisions of the ionized molecules with the cathodes can also cause sputtering of Ti and Ta from the cathodes which acts as a “getter” reacting with gas phase molecules to form solid phase compounds and thus removing gas from the system. The ion current between the cathode and the anode is related to the pressure of the system and can be used as a rough indicator of the pressure. Because this current is proportional to the pressure, operating this pump at higher pressures can cause excessive heating damaging the pump therefore care must be taken to ensure that this pump is only operating at sufficiently low pressures.

After pumping down a system from atmosphere and turning on the ion pump the pressure of a system is usually limited to $\sim 10^{-9}$ Torr. This is because the system accumulates layers of material, mostly water vapor, that absorb on its surfaces when the system is at atmospheric pressure and slowly outgas at low pressure. The amount can be limited by backfilling the chamber with dry nitrogen while bringing it to atmospheric pressure, but it is generally a significant problem regardless of the procedure used. To remove this material in a practical amount of time the system must be brought to high a temperature $>100 \, ^\circ C$, increasing the rate at which this material is desorbed from the surface. This procedure is commonly known as a bakeout. Heating is achieved in our system by wrapping resistive heating tapes around the chamber through which current is applied. The chamber is then wrapped with aluminum foil which confines hot air to circulate over the system. This keeps the temperature of the system even across its surface. Because the ion pump is usually operating during this procedure the temperature
must be increased gradually to ensure that the material doesn’t desorb too quickly and raise the pressure too high.

To increase the pumping speed of the system a TSP is used. The TSP is used alongside the ion pump and is not a replacement for it. This pump uses a titanium filament through which current is applied heating the filament and causing Ti to sublimate depositing a layer of Ti on the pump’s internal surface. As is the case in the ion pump, the titanium acts as a getter, reacting with gas phase molecules to form solid phase compounds, removing gas from the system. When the filament is heated molecules desorb from it, temporarily increasing the pressure of the system. The filament of the TSP is only turned on for about a minute and then turned off. When the system is at low pressure $<10^{-8}$ Torr the layer of Ti that was deposited can continue to remove gas for a number of hours.

To measure such low pressures a device known as a Bayard-Alpert gauge is used. This device uses the same principle through which the pressure can be obtained with an ion pump but is built to measure pressure rather than pump gases. High voltage is applied across an anode cathode pair resulting in the discharge of high energy electrons from the cathode. These electrons ionize gas phase molecules resulting in an ion current. The pressure will be proportional to this current and can be obtained with a proper calibration.

A clean leak tight system that has been baked out properly should be able to reach UHV pressures of $10^{-10}$ Torr. Ultimately the pressure will be limited by gas molecules defusing out from within the materials that make up the system or through the chamber walls and seals. During the manufacturing process in
stainless steel a significant amount of hydrogen is incorporated into the material. For UHV systems made of stainless steel, this hydrogen slowly defuses into the system and is the primary limiting factor for the pressure in these systems.

3.6 SAMPLE PREPARATION AND CHARACTERIZATION

3.6.1 Surface Preparation

This work involved three types of commercially obtained wafers. Sapphire wafers cut and polished to expose the (0001) surface and Si wafers with the (111) surface exposed. The Si wafers used for the growth of In films had very small miscuts while those used to prepare Si(111)-(4×1)-In had miscuts of ~2°.

The Si wafers were cut into rectangles with a length of 40 mm and a width of 7 mm. The samples were then degreased with methanol and quickly blown dry with nitrogen to avoid staining. The samples were then mounted to the sample holder to be placed in the UHV chamber.

After the UHV chamber reached UHV pressures the samples were outgassed by heating them to ~500°C with direct current for a few hours. The samples were then heated to ~1200°C for several seconds which results in a clean Si surface with a (7×7) reconstruction. In some of the experiments that took place this is the surface used for deposition of thin films. To produce the Si(111)-(√3×√3)-In approximately 2 ML of In was deposited on the surface followed by an annealing at 450°C for a few minutes.
To prepare a single domain Si(111)-(4×1)-In surface a Si(111) substrate with a small miscut of about 1.8° is used. The terraces resulting from the miscut are much larger than the Si(111)-(4×1)-In unit cell size and thus do not directly give rise to the reconstruction, instead the terrace steps align the In chains along just one of three equivalent crystallographic directions. This substrate was flashed at around 1250°C to clean the surface. It was then slowly cooled to 1050°C and quenched to 850°C where it was held for several minutes and then slowly cooled to room temperature. This procedure results in a uniform terrace structure [5]. About 1.8ML of In was deposited on the surface and annealed at 450°C resulting in the formation of a single domain Si(111)-(4×1)-In reconstruction [6, 7].

The sapphire substrates were purchased precut into 10 mm×10 mm squares. These samples were annealed in air in an alumina tube furnace at a temperature of 1500°C for several hours. The samples processed this way were scanned by an atomic force microscope (AFM) and found to have a uniform terrace structure. The samples were then held in a 40 mm×10 mm Mo structure by a tungsten clip. This structure could be mounted on the sample holder to be placed in the UHV chamber. When UHV pressures were reached the sample was outgassed using indirect heating from the tungsten filament which sits behind the sample. The sample was then annealed at 600°C using e-beam heating from the same filament; this procedure resulted in an aluminum terminated surface.

3.6.2 Thin Film Deposition

Thin film deposition was accomplished by molecular beam epitaxy (MBE). In MBE the material to be deposited is placed in a container or cell. The
material is heated by a filament which surrounds the cell to a temperature at which the material will have a substantial vapor pressure. A small opening at the top of the evaporator and facing the sample allows the material out of the cell. Because the system is kept at UHV the material does not scatter and travels in a beam to the sample where it condenses. The rate at which the material is deposited is dependent on the temperature of the cell. The temperature of the cell is therefore measured by a thermocouple and a temperature controller is used to control the amount of current flowing through the filament to keep the temperature constant. Layers of heat shielding material are used to insulate the cell. The cell must be made from a material that can withstand high temperatures and will not react with the evaporant.

The deposition rate can be measured by a crystal thickness monitor. This system oscillates a quartz crystal which is placed in the molecular beam. The resonance frequency of this oscillator will change as the quartz crystal acquires mass from material being deposited on it. This resonance frequency can be measured and the amount of deposited material can be deduced.

3.6.3 Atomic Force Microscopy

Atomic force microscopy (AFM) was used to image the surface of the sapphire substrates prior to the beginning of an experiment. For these measurements the AFM was used in tapping mode. In this mode a Si cantilever with a sharp tip at its end is oscillated near its resonance frequency just above the surface. A laser reflects off of the end of the cantilever and into a detector so that the frequency and amplitude at which the cantilever is oscillating can be
measured. A scanner lowers the tip until it lightly taps the surface. The amplitude of the oscillations will change depending on how close the cantilever is to the surface. The scanner then moves the cantilever in a direction parallel to the surface adjusting the height at which the cantilever is held to maintain a constant amplitude in its oscillations. By recording the heights over an array of points throughout a section of the surface an image of this part of the surface can be created. The scanner moves the cantilever using piezoelectric materials which expand and contract proportionally to an applied voltage.

3.6.4 Reflection High Energy Electron Diffraction

The UHV chamber at sector 33ID is equipped with a Reflection High Energy Electron Diffraction (RHEED) system. When making RHEED measurements high energy electrons, typically about 10keV in this work, strike the sample surface at grazing angles $\sim 3^\circ$ producing a diffraction pattern. The Ewald sphere will be much larger than the spacing between the surface diffraction rods so that a large portion of reciprocal space can be viewed at once. The system requires an electron gun to fire high energy electrons and a phosphor screen. The phosphor screen emits visible light when impinged upon by an electron allowing the diffraction pattern to be seen. Unlike in x-ray diffraction the electrons only penetrate a few atomic layers into the sample and so the diffraction pattern results purely from the surface. This system is generally used to determine the surface reconstruction and the surface quality. This can be done with x-ray diffraction but RHEED has an advantage in that it is quicker and doesn’t require beam time.
RHEED therefore can be used to aid in surface preparation prior to the beginning of an x-ray experiment.

3.7 DATA ACQUISITION

In order to carry out x-ray diffraction experiments the goniometer manipulates the sample and the detector so that the momentum transfer of the x-ray corresponds to some desired point in reciprocal space and the intensity is measured. The diffraction pattern resulting from the surface of a sample ideally is made up of infinitesimally thin rods as discussed in section 2.6. These rods however will have a finite width due to finite domain size and mosaicity in the film. Background intensity from sources such as Compton scattering and thermal diffuse scattering (TDS) also complicate the picture. Therefore to obtain the integrated intensity at a given point along a crystal truncation rod (CTR) the intensity across the width of the rod must be integrated and the background intensity of the rod must be obtained and subtracted.

The data presented in this thesis consist of reflectivity data and reciprocal space maps. When taking reflectivity data the in-plane components of the reflectivity are set to 0 and the x-ray intensity is taken at various values of the out of plane component of the reciprocal lattice vector. This is accomplished by holding $\delta = 0$ and manipulating $\mu$ and $\gamma$ so that $\mu = \gamma + \text{offset}$ where the $\text{offset}$ is the miscut angle. The reciprocal space maps were done simply by collecting the intensity in a mesh of points in reciprocal space. Two types of detectors were used
to collect data, scintillation detectors and CCD detectors. Furthermore two types of CCD detectors were used a large water cooled detector was mounted on the chamber table and was used to take reflectivity data. A smaller air cooled Pilatus CCD detector could be mounted on the detector arm and was used for reflectivity measurements. The reciprocal space maps were acquired with a scintillation detector. No background was taken, instead a background was assumed in the fit.

3.7.1 Acquiring Data with a CCD

When using the large water cooled CCD it is set on the \( \mu \) table and so moves with \( \mu \) but does not move independently. A long strip of the CCD, which extends across the range of outgoing angles that are to be taken, is exposed for each desired value of \( \mu \). The reflection will appear at a point in the exposed strip at a distance given approximately by

\[
x = d \tan(\mu)
\]

(3.4)

where \( d \) is the distance between the sample and the detector. A set of images of the reflected beam taken as \( \mu \) was increased and stacked on top of one another is shown in Fig. 3.7.
**Figure 3.7:** CCD images of the reflectivity, from a Pb film grown on sapphire, taken incrementally as $\mu$ is increased and stacked on top of each other. The CCD is mounted directly on the $\mu$ table. The total reflection can be seen at the top of the image, a forbidden sapphire peak is seen near the center and the Pb Bragg peak is seen near the bottom.
When using the Pilatus detector, the CCD is mounted on the detector arm. By moving $\gamma$ as $\mu$ is moved so that they are kept approximately equal the reflected beam can be kept in the center of the detector. A set of images of the reflected beam taken as $\mu$ and $\gamma$ were increased and stacked on top of one another is shown in Fig. 3.8.
Figure 3.8: The reflectivity, from an In film grown on Si, taken incrementally with a CCD as $\mu$ and $\gamma$ are increased and stacked on top of each other. The CCD is mounted directly on the detector arm. Each CCD image has been integrated vertically so that each row in the image results from a CCD image. In Bragg peaks are seen near the top and bottom of the image, a forbidden Si peak is seen near the center.
When taking the reflectivity with a CCD the background is interpolated for the image by taking a strip above and below the reflection and fitting the data there to a polynomial. This background can be subtracted and then the intensities throughout a window that encompasses the reflection can be summed to obtain the integrated intensity at the known point in reciprocal space.

3.7.2 Acquiring Data with a Scintillation Detector

For taking reflectivity data with a point detector the ridge scan method was used. In this technique the reflectivity is first taken in the same way that it is taken with the Pilatus detector. The \textit{offset} is then set to some nonzero value and the scan is repeated so that the scan runs alongside the reflectivity but the reflection does not enter the detector. Another scan is then done in which the \textit{offset} is set negative to the previous value. These two scan can then be averaged and taken as the background to subtract from the first scan.

REFERENCES


CHAPTER 4
MODULATED SILVER FILMS

4.1 INTRODUCTION

Thin metal films grown on semiconductor substrates have been a topic of prevailing interest for many years among the condensed matter community and in industry. One important step in comprehending these structures is to elucidate the role that the substrate interface plays on the properties of these films. The interface can provide a template for film growth which can have profound effects on the structure and properties of the film. This has been demonstrated in studies of metal films grown on substrates with V-shaped grooves [1], semiconductor wires [2] and miscut substrates with metallic wires [3--6]. Such structures have been shown to have properties such as enhanced giant magnetoresistance [1], modulation of photoluminescence spectra due to quantum confinement [2], ferromagnetism induced in atomic chains [4], a highly anisotropic metal-insulator transition at low temperature [5] and coherent grating cavity modes [6].

The atomic and electronic structure of Ag films, grown on an array of atomic In chains on Si(111), the Si(111)-(4×1)-In surface, commonly known as In(4×1), has been shown to be modulated by the underlying chains, in the direction perpendicular to them [7,8]. These modulations are found to persist in films with a thickness as great as 30 ML. Angle resolved photoemission (ARPES)
experiments carried out on this system showed that the electrons were confined by these modulations in quasi one dimensional states, providing evidence of a topological phase transition [8]. It was found by STM experiments that the unit cell of the Ag film in the modulated direction matches that of the substrate and it was proposed that a periodic stacking fault is induced in the system in order to relieve strain and make this possible [7]. In a later theoretical calculation it was found that a double stacking fault inserted into the unit cell can better reproduce the observed electron dispersion curves [9]. STM however only probes the surface of the film and so the stacking faults were not directly observed. In the present study the internal structure of the film is clarified by x-ray diffraction. We have taken reflectivity data to provide detailed information about the out of plane structure and reciprocal space maps to determine the structure of the unit cell of these films for a number of different coverages. The results of this study are shown to be consistent with the existence of a single stacking fault in the unit cell.

4.2 EXPERIMENTAL METHODS

Surface x-ray diffraction was used to characterize the Ag films. The x-ray diffraction experiments were conducted at the APS (Advanced Photon Source) beamline 33-ID-E using 19.9 keV x-rays. This experimental station contains a UHV chamber equipped with two MBE (Molecular beam epitaxy) evaporators so that the experiments could be conducted in-situ.
To prepare a single domain In(4×1) surface a Si(111) substrate with a small but substantial miscut of about 1.8° is used. A ball and stick model of the In(4×1) is shown in Fig. 4.1. The terraces resulting from the miscut are much larger than the In(4×1) unit cell size and thus do not directly give rise to the reconstruction, instead the terrace steps align the In chains along just one of three equivalent crystallographic directions. A cartoon in Fig. 4.2 shows how the chains propagate parallel to the steps.
**Figure 4.1:** Atomic model of the In(4×1) surface. The surface unit cell is highlighted by a red rectangle the unit cell of the modulated Ag film is shown in green.
Figure 4.2: Cartoon representing In chains on a miscut Si substrate. The chains run parallel to the edge of the substrate terraces chains that are crystallographically equivalent but do not run parallel to the terrace edge will be cut off by the edge.

The miscut Si(111) substrates were flashed at around 1250°C to clean the surface. They were then slowly cooled to 1050°C and quenched to 850°C where it was held for several minutes and then slowly cooled to room temperature. This procedure results in a uniform terrace structure [10]. About 1.8 ML of In was deposited on the surface and annealed at 450°C resulting in the formation of a single domain In(4×1) reconstruction [11,12]. The surface reconstruction was verified with RHEED. The sample was then cooled to ~160 K and Ag films were deposited on the reconstructed surface before the sample was allowed to warm to room temperature in order for the granular as-deposited films to recrystallize into a smooth film [7,13].
In order to describe positions in reciprocal space in the explanation of x-ray data a Si(111) surface coordinate system will be used as discussed in chapter 2. Due to the miscut, the Si(111) direction will not be perpendicular to the optical normal.

Two types of data were taken to be analyzed. Using a point detector reciprocal space maps were taken along the H direction from −1.7 to 0.4 and along the L direction from 0.9 to 1.9 at K=1.33.

Using a Pilatus CCD detector the images of the reflectivity in the Si(111) direction were taken at many values of L. The background was acquired by, interpolating from the strips above and below the reflection, and subtracted from the image. The image in Fig. 4.3 shows reflectivity images taken over a range of L values and stacked on top of one another each reflection has had its background removed and the rows of each image have been summed together so that there is a single row for each L value. The intensities over each image were then summed and multiplied by an appropriate geometrical factor [14]. Data was taken for films of different thickness using both techniques.
Figure 4.3: The reflectivity, from an 8 ML film grown on In-(4\times1), taken with a Pilatus CCD. Ag Bragg peaks are seen near the top and bottom of the image, a forbidden Si peak is seen near the center and a rod like feature extending from the forbidden Si peak in the optical normal direction is marked by a yellow arrow.
4.3 ANALYSIS

To model the data calculations of the intensity based on the single and double stacking fault model were considered. The intensities were calculated using the structure factors for the modulated and unmodulated Ag film, twinned domains for the Ag films were also included.

The atomic structure and the unit cell of the Ag film with the single and the double stacking fault model are shown in Fig. 4.4. (a)-(d) Ag film modulated by a single stacking fault will have a unit cell that can be described by the lattice vectors

\[
\mathbf{a}_{1,\text{film}} = 4\mathbf{a}_1 + 2\mathbf{a}_2; \quad \mathbf{a}_{2,\text{film}} = \frac{a_{Ag}}{a_{Si}}\mathbf{a}_2; \quad \mathbf{a}_{3,\text{film}} = \frac{a_{Ag}}{a_{Si}}\left(-\frac{1}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{3}\mathbf{a}_3\right) \quad (4.1)
\]

where \(\mathbf{a}_1, \mathbf{a}_2\) and \(\mathbf{a}_3\) are the basis vectors of the Si(111) surface unit cell and \(\mathbf{a}_{1,\text{film}}, \mathbf{a}_{2,\text{film}}\) and \(\mathbf{a}_{3,\text{film}}\) are the basis vectors of the modulated film. The reciprocal lattice vectors of such a crystal will then be

\[
\mathbf{b}_{1,\text{film}} = \frac{1}{4}\mathbf{b}_1 + \frac{1}{4}\mathbf{b}_3 \quad (4.2)
\]

\[
\mathbf{b}_{2,\text{film}} = \frac{a_{Si}}{a_{Ag}}\mathbf{b}_2 - \frac{1}{2}\mathbf{b}_1 - \frac{3}{2}\mathbf{b}_3 \quad (4.3)
\]

\[
\mathbf{b}_{3,\text{film}} = \frac{3a_{Si}}{a_{Ag}}\mathbf{b}_3 \quad (4.4)
\]

where \(\mathbf{b}_1, \mathbf{b}_2\) and \(\mathbf{b}_3\) are the reciprocal lattice vectors in the Si(111) surface coordinate system. The lattice vectors of a Ag film modulated by a double stacking fault will be
\[ \mathbf{a}_{1,\text{film}} = 4\mathbf{a}_1 + \left(2 - \frac{a_{Ag}}{2a_{Si}}\right)\mathbf{a}_2; \quad \mathbf{a}_{2,\text{film}} = \frac{a_{Ag}}{a_{Si}}\mathbf{a}_2; \quad \mathbf{a}_{3,\text{film}} = -\frac{1}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{3}\mathbf{a}_3 \] (4.5)

and its reciprocal lattice vectors will be

\[ \mathbf{b}_{1,\text{film}} = \frac{1}{4}\mathbf{b}_1 + \frac{1}{4}\mathbf{b}_3 \] (4.6)

\[ \mathbf{b}_{2,\text{film}} = \left(1 - \frac{a_{Si}}{2a_{Ag}}\right)\mathbf{b}_1 + \frac{a_{Si}}{a_{Ag}}\mathbf{b}_2 + \left(1 - \frac{3a_{Si}}{2a_{Ag}}\right)\mathbf{b}_3 \] (4.7)

\[ \mathbf{b}_{3,\text{film}} = \frac{3a_{Si}}{a_{Ag}}\mathbf{b}_3 \] (4.8)

The positions of some of the crystal truncation rods for single stacking fault model are shown in Fig. 4.4(e) and for the double stacking fault model in Fig. 4.4(f) along with the positions of the Si(111) and In(4×1) rods. For a film with the single stacking fault structure at \( K = a_{Si}/a_{Ag} = 1.33 \) there should be rods located at \( H = \frac{1}{2}n - a_{Si}/\left(2a_{Ag}\right) \) and in the double stacking fault model they will be located at \( H = \frac{1}{4}n - a_{Si}/\left(2a_{Ag}\right) + \frac{1}{8} \) where \( n \) is an integer. The x-ray intensities mapped at \( K = 1.33 \) for a 5 ML film are shown in Fig. 4.5 and peaks were found at \( H = -1.415, \quad H = -1.165, \quad H = -0.915, \quad H = -0.415, \quad H = -0.165 \) and \( H = 0.085 \) which are where they would be expected for a Ag film modulated by a single stacking fault. Additional peaks were found at \( H = -1.33 \) and \( H = 0 \) which would be where crystal truncation rods would be expected in an unmodulated Ag film which forms in a bulk like manner. There were no peaks found corresponding to the double stacking fault model indicating that a significant amount of this structure was not present.
The structure factor of the film will be

\[
F_{\text{mod}} = f_{\text{mod}} \left( 1 + e^{2\pi i \frac{a_{Si}}{a_{Si}} (H' + K')} + e^{2\pi i \frac{a_{Si}}{a_{Si}} (2H' + K')} + e^{2\pi i \frac{a_{Si}}{a_{Si}} (3H' + 2K')} + e^{2\pi i \frac{a_{Si}}{a_{Si}} (4H' + 2K')} \right)
\]

(4.9)

where the coordinate system is rotated to compensate for the tilt in each facet so that \( H' = (H + K/2) \cos(3.4^\circ) - K/2 + L \sin(3.4^\circ)/(2\sqrt{2}) \) and \( K' = K \). The structure factor for a film with the double stacking fault structure can be calculated similarly. The bulk like film will only have one atom in its unit cell and so its structure factor will simply be 1. The scattering amplitudes of the films can then be calculated using Eq. 2.43.
Figure 4.4: (a) (b) Front and (c) (d) top views of the atomic structure for the single and double stacking fault models. The different colored circles represent different stacking planes. Stacking faults are indicated by arrows. The solid and dashed lines show the unit cell of the modulated Ag film and the \( \text{In-}(4\times1) \) respectively. (e) in-plane reciprocal lattice sites for the single and (f) double stacking fault models. \( \text{Si}(111) \) lattice sites are represented by large green circles \( \text{In-}(4\times1) \) are in red unmodulated Ag film in yellow and modulated Ag film in blue.
To fit the data a distribution of thicknesses was assumed to be present in the film and the intensity from each thickness was added coherently so that no coherence factor was considered in order to limit the number of parameters. The film was assumed to be composed of modulated and bulk like film with twinned domains of each included. The intensity from each type of film was assumed to add incoherently and so the x-ray intensity will be proportional to a linear combination of the intensities from each type of film present in the system

\[ I = f_{\text{mod}} I_{\text{mod}} + f_{\text{unmod}} I_{\text{unmod}} + f_{\text{mod, twinned}} I_{\text{mod, twinned}} + f_{\text{unmod, twinned}} I_{\text{unmod, twinned}} \]  

(4.10)

where \( f_{\text{mod}} \) and \( f_{\text{mod, twinned}} \) are scaling factors for the modulated film and its twin and \( f_{\text{unmod}} \) and \( f_{\text{unmod, twinned}} \) those for the bulk like Ag film. In Fig. 4.5 the reciprocal space map data is compared to an unmodulated Ag film in Fig. 4.5(b) a fit based on a mixture of unmodulated film and film with a single stacking fault Fig. 4.5(c) and with a double stacking fault Fig 4.5(d). Only the film with the single stacking fault reproduces the correct peak positions.
Figure 4.5: (a) X-ray intensity in a reciprocal space map from $H = -1.7$ to 0.4 and $L = 0.9$ to 1.9 for $K = 1.33$ through the Ag rods along the red dashed line as seen in FIG. 4.4. (b) calculation based on an unmodulated Ag film growing in the [111] direction which includes twinned domains. (c) A fit which includes a mixture of unmodulated Ag film and Ag film which follows the single stacking fault model. (d) A calculation which includes the double stacking fault model.
Only the model which includes single stacking faults reproduces the correct peak positions.

Fitting of both the reflectivity and reciprocal space maps were carried out using the single stacking fault model. The reflectivity was calculated by taking into account the intensity from a mixture of modulated and unmodulated film and the In(4×1) substrate. Scaling factors for the modulated and unmodulated films, relaxation in the layering and layer occupancies were all allowed to vary. The calculated intensity was convoluted by a Gaussian in order to account for the small range of \( L \) values the CCD accepts at each data point. Experimental reflectivities and the best fit model are shown in Fig. 4.6.
Figure 4.6: Integrated Intensities of reflectivities with corresponding fits based on the stacking fault model. Film coverages are shown above each curve.

In order to fit the reciprocal space maps a polynomial background term, scaling factors for the modulated, unmodulated, twinned and untwinned films, relaxation in the layering in the in-plane direction, relaxation in the unit cell and an attenuation factor were all allowed to vary. Vertical layer relaxations and layer
occupancies found in the fit of the reflectivity were used. Fitting results for 6, 8, 12 and 15 ML films are shown in Fig. 4.7. A significant proportion, between 50 and 60%, of the unmodulated film was found to be present in these films. The percentage of twinned domains covering the surface decreased, from about 33% for the 5 ML film to about 5% for the 15 ML film, as the thickness increased.
Figure 4.7: Experimental and calculated (best fit) reciprocal space maps in the H-L plane with $K = 1.33$ for 6 ML, 8 ML, 12 ML and 15 ML films. The data shows peaks corresponding to the modulated film in both the twinned and untwinned orientations. Peaks corresponding to an unmodulated Ag film growing in the (111) direction are also observed indicating a significant admixture of this structure.
4.4 CONCLUSIONS

In conclusion single and double stacking fault models have been proposed to explain the structure of Ag films grown on In\((4\times1)\) substrates. We have used reciprocal space maps and reflectivity scans by x-ray diffraction to obtain information about the 3-dimensional internal structure of the films. The single stacking fault model is clearly superior to the double stacking fault model to explain our experimental results and is shown to provide an adequate fit to them.

REFERENCES


CHAPTER 5
LEAD FILMS ON SAPPHIRE

5.1 INTRODUCTION

The confinement of electrons in metal films by a substrate at the interface and the vacuum at the surface results in quantum well states. The electronic structure of these states is determined by the film properties, such as the film thickness and the potential barrier between the film and the substrate. The fact that the electrons are in these states however can cause drastic differences in the properties of these films as compared to their bulk counterparts. These differences are known as quantum size effects (QSE). The Fermi wavelength is a determining factor in these QSEs and can cause the properties of such films to oscillate as the film thickness is increased with a period of the Fermi wavelength divided by two [1]. This period of oscillation is approximately equal to the thickness of 2 ML of Pb grown in the (111) direction. The properties of Pb films would therefore be expected to oscillate in a bilayer fashion. Furthermore the conduction electrons in Pb behave very much like free electrons which in some cases make it relatively easy to model the properties of these systems. Pb films grown on Si substrates have proven to be an ideal system to study these QSEs, and so a plethora of research has been done on these systems resulting in the observation of a number of QSEs such as preferred film thicknesses and changes in the superconducting...
transition temperature [2-8]. This research has resulted in a deep understanding of QSEs.

The potential barrier between the substrate and the film determines how much charge from the free electrons in a thin metal film spills into the substrate. By manipulating this barrier it would reasonable to assume that the QSEs in the system could be modified as well. To do this different surface reconstructions could be considered, however to drastically change the barrier a different substrate should be used. Using an insulator would significantly increase the barrier and decrease the amount of charge spilling into the substrate; however smooth thin metal films are generally difficult to grow on insulator substrates. Insulators such as oxides in many cases have a low surface energy and metal overlayers generally do not wet the surface resulting in the growth of rough films. Sapphire surfaces have received a fair amount of attention in the literature and were selected as the substrates used in the experiments discussed here. It was determined through this study that, although rough, Pb films can be epitaxially grown on sapphire substrates and that QSEs can be observed in this system.

5.2 EXPERIMENTAL DETAILS

The x-ray diffraction experiments conducted for this work were carried out in the surface diffraction station at beamline 33ID at the Advanced Photon Source at Argonne National Lab. The x-rays used were tuned to an energy of 19.9 keV.
The sapphire substrates were annealed in a tube furnace at 1500°C for several hours in air. This treatment has been shown to result in a surface terminated by well-ordered terraces with steps that are 6 sapphire layers high. AFM images, such as the one shown in Fig. 5.1 were taken after annealing and the substrates used in these experiments were found to have similar surfaces. The substrates were mounted in the UHV chamber and then cleaned by an annealing at 600°C for 30 minutes which results in an aluminum terminated surface [9]. The resulting surface produced a distinct x-ray reflectivity. After a Pb film was deposited the surface could be regenerated by annealing the substrate at 600°C to desorb the Pb and an identical reflectivity could be obtained. This reflectivity was consistent with a sapphire substrate terminated by 2 ML of Al.
Figure 5.1: The AFM image of a treated sapphire substrate shows a well-defined terrace structure.

The sample was cooled to low temperature, by a liquid nitrogen cold finger, for Pb deposition. The Pb was deposited onto the substrate using an MBE system with a pyrolitic boron nitride crucible. The sample was then annealed slowly to higher temperatures at first using a filament that was placed behind the sample and then by bombarding the sample with electrons from the same filament to obtain higher temperatures. The x-ray reflectivity of the samples was measured during deposition and annealing using a CCD detector to take data in real time. After deposition and at incremental points during annealing the reflectivity was measured using a point detector using the ridge scan method discussed in section
3.6. The reflectivities taken with the point detector cover a wider range of reciprocal space however the reflectivities taken using both techniques have a wide enough range that QSEs can be observed.

5.3 ANALYSIS

The x-ray reflectivity can be used to determine the structure of the film in the direction perpendicular to the surface. The preferred thicknesses of these films are therefore accessible to this technique and this is the QSE of interest to this study. For the Pb on Si system the Pb forms a wetting layer on the Si surface and the island heights are sometimes stated as the number of layers above the wetting layer. The true number of layers will therefore be the quoted number of layers plus one in those cases. The preferred heights in this system are an odd number of layers at lower coverages 5, 7 and 9 but switch to even at higher coverages 12, 14 and 16.

To model the x-ray reflectivity data the standard kinetic model described in chapter 2 was used. The intensities were calculated from Eq. 2.47 using the structure factor for sapphire for the substrate which is given by Eq. 2.45. As discussed in the section above it was found that the treatment used to prepare the sapphire substrates resulted in the substrates being terminated by two layers of aluminum with a density that was roughly that of bulk aluminum. The distance between the last oxygen layer and the first of the two aluminum layers, the distance between the two layers and the density of the layers were all allowed to vary. Introducing a term
to the scattering amplitude of the substrate, where \( p_i \) is the density of each layer and \( d_i \) the distance from the origin in multiples of the out of plane surface coordinate of sapphire. It was found that introducing lattice relaxations in the Pb film did not significantly alter the results and therefore they were not introduced into the final model for fitting the reflectivity data. The scattering amplitude for the Pb films was given by Eq. 2.41

Both coherent and incoherent sums over the distributions of islands with different thicknesses were considered and so Eq. 2.46 was used to calculate the intensities.

### 5.4 RESULTS AND DISCUSSION

Films were grown at various temperatures and the reflectivity was taken during growth. Reflectivity data, for several thicknesses, taken during deposition at \(-100^\circ\text{C}\) are shown in Fig. 5.2(a) where the strong peaks at \( L = 4.5 \) correspond to the Pb Bragg peak position and the smaller peaks that show up throughout the data are interference fringes. The corresponding thickness distributions are shown in Fig. 5.2(b). If the thickness distribution were random the interference fringes would be washed out near the anti-Bragg peak position at \( L = 2.25 \), however it has been well established that for a film with bilayer oscillations the fringes near this point are enhanced. It can be seen from the data that there is such an enhancement present in this case. The quoted thicknesses are
taken from the amount deposited assuming a deposition rate that was previously obtained by a crystal thickness monitor. The average island thickness is significantly larger than the thickness deposited indicating that the Pb does not wet the surface and much of the substrate remains uncovered. Islands with an even number of layers show a tendency to have greater populations than their neighbors, and so a preference for these islands is already evident upon deposition.
Figure 5.2: (a) The integrated intensity of the reflectivity taken for several different coverages shown above each curve taken during deposition at \(-100^\circ C\). (b) The corresponding island height distribution for each reflectivity.

The reflectivity of a 5 ML film deposited at \(-164^\circ C\) is shown in Fig 5.3(a) with that for the same film annealed to \(-25^\circ C\) and \(200^\circ C\). The corresponding thickness distributions are shown in Fig. 5.3(b). Even upon deposition at \(-164^\circ C\) islands with a number of layers \(N=8\) and \(N=10\) have a greater population than those with \(N=9\), and so the preference for an even number of layers is already apparent. As the sample is annealed the island height
distribution shifts toward thicker films. At \(-25^\circ \text{C}\) the dominant thicknesses are 10 and 12 ML and at \(200^\circ \text{C}\) they are 12 and 14 ML.

\[\text{Figure 5.3: } \text{(a)} \text{ The integrated intensity of the reflectivity taken for a 5 ML film taken incrementally at annealing temperatures of } -164^\circ \text{C}, 25^\circ \text{C} \text{ and } 200^\circ \text{C} \text{ (b)} \text{ The corresponding island height distribution for each reflectivity.}\]

Reflectivities taken incrementally during the annealing of a 5 ML film deposited at \(-50^\circ \text{C}\) and annealed to \(270^\circ \text{C}\) are shown in Fig 5.4 with their corresponding thickness distributions. This data also shows a preference for an even number of layers. This preference persists up to \(250^\circ \text{C}\) and finally
disappears at 270° C where the fringes are washed out and the distribution of thicknesses becomes featureless.

**Figure 5.4:** (a) The integrated intensity of the reflectivity taken for a 5 ML film taken incrementally at several annealing temperatures. (b) The corresponding island height distribution for each reflectivity. Bilayer oscillations are found to persist as high as 250°C

Compared to the Pb/Si(111) system the Pb films grown on sapphire are much rougher [1, 2, 6, 10] and so the structure of the fringes in the reflectivity is not as well defined, features of bilayer oscillations however can be observed and the data could be fitted to show a preference for islands with an even number of
layers. In the Pb/Si(111) system the preferred island heights are odd at low coverage 5, 7 and 9 ML but switch to even at higher coverages 12, 14 and 16 ML. This occurs because half of the Fermi wavelength is \( \sim 2.2 \) ML and not exactly 2 ML causing the preferred thickness to beat between even and odd with a period of approximately 9 ML. The preferred thicknesses found in this study were all even and so this beating pattern was not observed over the coverage range studied in this work. It is possible that the small diameters of the islands in this system caused the lattice to contract laterally resulting in a vertical expansion of the lattice. A small increase in the layer spacing could dramatically increase the beating period and an increase of \( \sim 2\% \) could eliminate it all together.

The most intriguing difference between these systems is the temperature range over which the island height preference is observed. For the Pb on Si system this effect disappears at around room temperature. For the Pb on sapphire system bilayer oscillations in the preferred thickness is observable up to \( 250^\circ C \). In terms of absolute temperature this critical temperature \( T_c \) is nearly twice as high. For a system where the entire valence band of the film lies within the band gap of the substrate so that the electrons in the system are completely confined, the variation in the surface energy as a function of film thickness will be on the order of the valence band width \( \delta E \sim W/N \). The Pb on Si system is only partially confined and the differences in energy for different film thicknesses have been found to be on the order of \( 0.6 \) eV \[10, 11\]. The energy difference for different thicknesses in Pb on sapphire is \( \approx 2 \) eV \[12\]. Preferred thicknesses will cease to exist when the thermal energy \( k_B T \) is near the difference in energy for different
island heights. This energy for Pb on sapphire is therefore approximately 3 times that for Pb on Si. This is in reasonable agreement with our observation of a critical temperature twice as high in the Pb on sapphire system.

Diffusion of atoms on the surface is a necessary condition for island ordering. Reciprocal space maps around the Bragg peaks reveal a tube running parallel to the crystal truncation rods in reciprocal space. These features result from island ordering in the system that is isotropic but radially ordered [13-16]. The average interisland distance will be \( D = 2\pi/R \) where \( R \) is the radius of the tube in reciprocal space. Transverse cuts through these tubes for several different film thicknesses, taken during the growth of a film at are shown in Fig. 5.5(a), here the central peaks are the Bragg peaks and the shoulders are cuts through the tube. The interisland distance as a function of film thickness is shown in the inset of Fig 5.5(a). It is clear that the self-organization of islands occurs at \(-100^\circ C\). The shoulders are evident even at 1.5 ML where the interisland distance is \( \approx 100\text{Å} \). The interisland distance can be seen to increase as Pb is deposited onto the film implying that the islands coalesce as they grow the distance is \( \approx 900\text{Å} \) at 10.4 ML. Similar data taken during the annealing of a 5 ML film is shown in Fig 5.5(b). An increase in the interisland distance is also clear during annealing but is much less dramatic. The distance increases from about \( 300\text{Å} \) to \( 500\text{Å} \) during an annealing from \(-50^\circ C \) to \( 270^\circ C \). In comparison to Pb on Si the interisland distance is much smaller implying smaller island sizes [14].
Figure 5.5: (a) Tranverse cuts in reciprocal space through tubes surrounding the Pb Bragg peaks for several Pb coverages. The distance between the peaks on either side of the Bragg peaks is indicative of the interisland distance of the Pb islands. The inset shows the interisland distance as a function of coverage. (b) similar cuts taken at different annealing temperatures

5.5 CONCLUSIONS

Although Pb films grown on sapphire substrates are rougher than those grown on Si intriguing differences in the properties of these system have been found, demonstrating the importance of the interface in quantum well systems. A change in the phase of the quantum oscillations is induced by the substrate. Most
importantly the confinement gap of the substrate is found to play a key role in determining the thermal stability of these films. For thin film engineering applications where thermal stability is a key requirement, such insight may prove useful.

REFERENCES


CHAPTER 6

INDIUM FILMS ON SILICON

6.1 INTRODUCTION

In the previous chapter Pb films grown on sapphire substrates were compared to Pb films grown on Si substrates and significant differences were found in the properties of the films demonstrating the importance of the interface on the properties of thin films. In the present study thin films composed of a material with significantly different electronic properties than lead are considered, namely indium. The primary reason to expect an interesting contrast between films made of indium and lead is that the period of oscillations in the standard quantum well state model is \( \Delta N = \frac{\lambda_f}{2} = 3.3 \) for indium. It is therefore reasonable to expect that trilayer oscillations may be observed in the properties on indium thin films with occasional 4 ML leap layers as opposed to the bilayer oscillations that have been observed in lead thin films.

Although Pb has been the material of choice for studying quantum size effects in metal on insulator systems, there has been a substantial amount of work done on In films [1-12]. The superconducting transition temperature of a single layer of indium on Si(111) the \( \text{Si}(111)-\left(\sqrt{7} \times \sqrt{3}\right)-\text{In} \) surface has been measured and found to be quite close to the bulk value [7]. In the case of Pb significant differences in the transition temperature for thin films and the bulk have been
observed making indium an intriguing material to compare to lead. Tri-layer oscillations in the electrical and optical conductivity of In have been observed. An STM study on indium films grown on Si(111)-(\(\sqrt{3} \times \sqrt{3}\))-Pb has shown a preference for 4 ML films in films grown at low temperatures [8]; however In films have been observed to grow in a layer by layer manner beyond 7 ML [2-4]. In an ARPES study of In films grown on Si(111)-(\(\sqrt{3} \times \sqrt{3}\))-In, referred to here as \(\sqrt{3} \times \sqrt{3}\), a preference for 4 ML was again observed along with a preference for 7 ML demonstrating tri-layer oscillations in the preferred thickness for these films [6].

In the present study indium films grown at low temperature on Si(111)-(7×7) and \(\sqrt{3} \times \sqrt{3}\) are studied with surface x-ray diffraction and the preliminary results of the study given. The dominant thickness in the films are deduced from counting the interference fringes. A 10 ML film grown on a \(\sqrt{3} \times \sqrt{3}\) surface is annealed to higher temperatures and upon annealing a preference for 13 ML appears to exist.

6.2 EXPERIMENTAL DETAILS

The x-ray data for this work was taken at the advanced photon source at sector 33-ID-E. This station is equipped with a UHV chamber with an MBE effusion cell so that the experiments could be carried out in-situ. In films were grown on two different types of Si surfaces, a clean 7×7 and the \(\sqrt{3} \times \sqrt{3}\)
surface. To make the sample used in this experiment a 40 × 10 mm rectangle was cut from a commercial P-doped Si wafer. The sample was mounted on a liquid nitrogen cooled manipulator. The sample was thermally anchored to the manipulator by a sapphire block. Two thermocouples placed near each side of the sample were used to measure the temperature which was found to be near the average of the two when calibrated. Tantalum foils wrapped around each side of the sample provide electrical contacts so that the sample can be heated by running current directly through it and a tungsten coil placed behind the sample allows indirect heating. Both surfaces were prepared by outgassing the sample for a few hours and flashing the sample at about 1200°C, by running current directly through the sample, to create a clean 7×7 surface. To produce the $\sqrt{3} \times \sqrt{3}$ approximately 2 ML of In was deposited on the surface followed by an annealing at 450°C for a few minutes. The quality of both surfaces were verified by reflection high energy electron diffraction (RHEED) and the annealing time for the $\sqrt{3} \times \sqrt{3}$ surface was determined so that there were no traces of Si-(111)-(4×1)-In or Si(111)-($\sqrt{3} \times \sqrt{3}$)-In present in the RHEED pattern. Indium films were deposited at a rate of 0.75ML/min with the substrate temperature held at around 135 K. So that data for many different film thicknesses could be obtained additional Indium was deposited incrementally onto existing films. After reaching a certain thickness the films were then annealed using a tungsten filament mounted behind the sample after reaching the desired temperature the sample was allowed to cool again and the reflectivity was taken for a number of annealing temperatures.
These experiments utilized 19.9 keV x-rays from the undulator source at sector 33-ID. X-ray reflectivity and crystal truncation rod (CTR) data were taken using a Pilatus CCD detector. For the reflectivity data images were taken at a number of different incident angles. The background intensity was interpolated from two strips above and below the reflection this background intensity was subtracted from the image. The value obtained by summing over each image and multiplying by the appropriate geometrical correction factors was taken as the integrated intensity at the given point in reciprocal space.

![Figure 6.1](image)

**Figure 6.1:** (a) Integrated intensity of the reflectivity taken from In films grown on 7×7 surfaces and (b) $\sqrt{3} \times \sqrt{3}$ for coverages indicated above each curve.

Reflectivity data for several coverages of In films grown on 7×7 and $\sqrt{3} \times \sqrt{3}$ surfaces are plotted in Fig. 6.1(a) and (b) respectively as a function of the out of plane momentum transfer in Si(111) reciprocal lattice units. Even for
the 10 ML film peaks from the \(7\times7\) could be found. A few of these peaks are seen in Fig. 6.2 where the x-ray intensity is scanned in the \(K\) direction for \(H = 0\) and \(L = 0.25\). It is possible that the persistence of the \(7\times7\) at the interface has a significant effect on the growth of the In films complicating their structure.

![Graph showing X-ray intensity as a function of K for H = 0 and L = 0.25, taken for In films of coverages of 7 ML and 10 ML grown on a 7×7 surface. Peaks from the 7×7 are found to persist upon burial by an In film.](image)

**Figure 6.2:** X-ray intensity as a function of \(K\) for \(H = 0\) and \(L = 0.25\), taken for In films of coverages of 7 ML and 10 ML grown on a 7×7 surface. Peaks from the 7×7 are found to persist upon burial by an In film.
6.3 ANALYSIS AND DISCUSSION

By counting the number of fringes between the Bragg peaks and adding two as discussed in section 2.6 the dominant thickness in a thin film can be obtained. As In is added to the film the dominant thickness taken from the number of fringes increases fairly smoothly from 6 ML in the reflectivity with the lowest coverage to 7 and 9 ML as the coverage is increased. In the film with the highest coverage the fringes are difficult to discern near the anti-Bragg peak. If the fringes are assumed to be approximately evenly spaced the dominant thickness will be between 10 and 11 for this film. This smooth increase suggests that the film is growing in a roughly layer by layer manner for these coverages.
Figure 6.3: The integrated intensity of the reflectivity taken for several different coverages shown above each curve. The fringes are marked with arrows and the first and last fringe between the In Bragg peaks is numbered for each reflectivity.

As the films are annealed from room temperature to temperatures over 200°C the number of fringes increases so that the dominant thickness appears to be around 13 ML. This implies a strong preference for 13 ML.
Figure 6.4: The integrated intensity of the reflectivity of a 10 ML film taken at a few annealing temperatures shown above each curve. The fringes are marked with arrows with the first and last fringe between the In Bragg peaks numbered for each reflectivity.
6.4 CONCLUSIONS

Previous studies have shown preferences for coverages of 4 and 7 ML for In films. These were not observed in this study and it is likely a more thorough study of the annealing behavior of films with lower coverages will be needed to observe this effect. Although no preferred thicknesses have been previously found in films with a coverage of greater than 7 ML this study suggests that when thicker films are annealed a substantial preference for 13 ML in thickness can be observed. Further analysis will need to be carried out to confirm these results.

REFERENCES


CHAPTER 7

CONCLUSIONS

Three experimental investigations have been presented in this dissertation. We have studied Ag films grown on a Si(111)-(4×1)-In surface, Pb films grown on sapphire substrates and In films grown on Si substrates.

Ag films grown on In(4×1) surfaces have been shown to be modulated by the underlying substrates. A single stacking fault and a double stacking fault model have been proposed as the modulated structure. The SXRD experiments carried out as part of this thesis show that the films have the single stacking fault structure.

Pb films grown on Si(111) substrates have been an archetypal system for studying the effects of electron confinement in thin films. In this work a study of Pb films grown on sapphire substrates is presented so that the effects of increasing the potential barrier at the substrate can be examined. As in the Pb on Si case bilayer oscillations in the preferred heights of islands in the thin films are observed. Unlike the Pb on Si system however no beating pattern is observed in these bilayer oscillations, within the range of thicknesses studied, implying that the periodicity of the beating pattern is much longer in this system. Most interestingly the thermal stability of the preferred islands in the system is shown to be much more robust than in Pb on Si demonstrating the importance of the
potential barrier at the substrate in stabilizing films against thermal fluctuations that can roughen it causing a random distribution of island heights.

In the final experiment presented as part of this work In films grown on Si(111) substrates are studied. In films were grown on Si(111)-(7×7) and Si(111)-(√3×√3)-In surfaces. Significant differences in the resulting reflectivity were observed. After burial by In films the 7×7 was found to persist. Previous studies have shown trilayer oscillations in the thickness dependence of some of the properties in this system. Preferred thicknesses of 4 and 7 ML have previously been observed with layer by layer growth occurring at greater coverages. In the SXRD discussed here experiments discussed here these preferred thicknesses were not observed and a more careful study of coverages near these may be needed for a detailed understanding. By annealing films with greater coverages however islands of a preferred height of 13 ML were apparent, in the films grown on the √3×√3 surface, suggesting that this quantum size effect can be observed in this system for higher coverages.