X-RAY DIFFRACTION STUDIES
ON THE Pb/Si(111) SYSTEM

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Doctor of Philosophy

by
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X-RAY DIFFRACTION STUDIES
ON THE Pb/Si(111) SURFACE

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Dedication

I would like to dedicate this dissertation to everyone that supported me, in spite of myself. I would like to thank my family. I would like to thank my advisor, Paul, who in encouraged me to become better. Even when it required a swift kick, rather than a pat on the back. Mostly, I would like to dedicate this to Sarah, my love. Veni, Vidi, Vici.
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ABSTRACT

The Pb/Si(111)7x7 system has attracted considerable interest because it exhibits novel Quantum Size effect islands (QSE). Initial Pb atoms on the surface form a continuous wetting layer, followed by island formation with flat tops and discrete heights. Moreover, certain discrete heights are preferred over others. Because of the discrete height preference, islands which do not have the preferred heights decay and contribute to growth of islands with preferred heights at a rate which is significantly faster than Pb-crystals studied in other systems. The fast rate is even more surprising because Pb atoms from decaying islands must transport across the continuous wetting layer before reaching more stable islands. Understanding the fast transport across the wetting layer has motivated this study to determine the structure of the wetting layer.

This dissertation investigates the structure of the Pb wetting layer on the Si(111)7x7 using X-ray diffraction techniques. It was found that the wetting layer shows a surprising kinetic behavior within the structure over a ∼200°C temperature range. When grown at low temperature (<150°C), the wetting layer structure increases its order from an initial deposited structure toward an 8x8 lattice. However, when grown at higher temperatures (>150°C), the wetting layer and the Si(111)7x7 transition to a Pb lattice gas on the Si(111)1x1 surface, removing the 7x7 reconstruction. Moreover, the rate of transition also increases with temperature. These kinetic observations resulted in a surface preparation procedure for a stable Pb/Si(111)7x7 wetting layer.

The structure of the stable Pb/Si(111)7x7 wetting layer was solved with X-ray scattering. The samples were prepared and studied in ultrahigh vacuum (in-situ) using synchrotron radiation at the Advanced Photon Source, on the 6IDC beamline. The scattering
measurements were a combination of reflectivity, in-plane diffraction, and truncation rod geometries.

The structure of the Pb/Si(111)7x7 has two Pb layers along with a modified Si adatom layer. The wetting layer is densely packed, with atoms distributed between bulk Si sites and a lattice of commensurate 8x8 sites. Directly below the wetting layer is a low density, ~6 Pb atom, Pb layer occupying sits directly above Si 7x7 atoms. The 12 atoms in the initial Si 7x7 adatom layer are displaced toward the edges of the unit cell, in the presence of Pb. Moreover, they maintain a 6x6 distance commensurate with the 7x7 unit cell. The structural model proposed here addresses conflicting models that appear in the literature and it solves a long-standing problem that is important to quantum size effect systems.
Chapter 1

Introduction

There has been great interest over the last several decades into the area of nano-scale device design. Consistent breakthroughs in design of nano-scale transistors continually push the boundaries of our understanding of physical laws. Interestingly, new physical considerations that have been observed at the nano-scale, such as electron wave confinement. Electron confinement modifies classical physical theories and leads to new effects, known as Quantum Size Effects (QSE). Observations with Metal-Semiconductor systems have shown to exhibit some unique QSE, such as island growth with discrete heights and novel coarsening times [1, 2]. Here, we will describe our work on the Pb-Si(111) Metal-Semiconductor system and the insights it provides into the QSE physical phenomena.

The growth of Pb on Si(111) represents an ideal system for exploring the physical phenomena on the nano-scale because Pb is immiscible with Si. Consequently, Pb grows on top of the substrate by first forming a complete wetting layer followed by island growth, which is a classical growth mode called Stranski-Krastinov (SK). Unlike classical SK growth where large hemi-spherical crystals grow on the wetting layer, Pb islands are observed
to exhibit discrete height preferences on the surface [3]. The discrete height preferences have been modeled as an interesting Quantum Size Effect property of the system [4, 5]. The models can accurately predict the discrete island heights as well as the experimentally observed bi-layer stable 5,7,9-layer heights.

Pb islands further deviate from classical behavior when observing their coarsening on the surface. Initial Pb island formation creates a distribution of discrete island heights, instead of only forming the bi-layer stable heights predicted. However, the island heights which are not bi-layer stable decay and contribute to the islands which are preferred. Classical coarsening theory suggests that the island decay process follows a power law behavior called Ostwald Ripening, where all islands will eventually decay to a single stable island. Pb islands do exhibit the power law decay expected. However, the islands do not converge to a single island as Ostwald ripening predicts [2]. Furthermore, the islands decay rate is orders of magnitude faster than had been observed in larger Pb crystals [6, 7].

The fast coarsening times are further surprising when considering the required Pb atom diffusion process on the surface. As a part of SK growth, Pb islands coincide with a continuous wetting layer between then. As islands decay, Pb atoms from an unstable island must diffuse across the wetting layer toward a stable island. Consequently, the diffusion across the wetting layer complicates the fast coarsening times, because Pb atoms must hop across possible wetting layer binding sites to reach stable islands. Therefore, the structure of the wetting layer plays an important role in understanding the fast coarsening process of Pb islands.

The Pb wetting layer structure has been a long standing problem, with multiple proposed structural models. The wetting layer was initially studied with X-ray diffraction, and a proposed model suggested the wetting layer was densely packed with Pb atoms occupy-
ing an 8x8 lattice on the surface [8, 9]. Later studies using STM techniques suggested that Pb atoms conform to the Si(111)7x7 surface and occupy sites directly above Si atoms [10].

The problem was further complicated because the wetting layer surface preparation was inconsistent between the two different studies. These two mutually exclusive models have left an open question regarding the exact structural model of the wetting layer.

We studied the Pb/Si(111) wetting layer structure using X-ray scattering. X-ray scattering is an effective tool for this study because it can probe buried surface and interface structures which are difficult or impossible to observe with other techniques (such as AFM, STM, or LEED). Also, X-ray scattering provides statistical information on the atomic length scale which real space techniques cannot provide. We utilized the high intensity X-ray source at the Advance Photon Source (APS) located at Argonne National Labs (ANL). The APS X-ray source provides the necessary intensity to observe surface structures which lab sources would not be capable of observing.

In this study, we have resolved a structural model on a stably grown wetting layer based on X-ray scattering. The wetting layer shows an interesting kinetic behavior which changes the structure of the layer over a ∼200°C temperature range [11]. The kinetic observations provide a surface preparation method, which is necessary to create a stable and reproducible wetting layer structure. The stable wetting layer structure was then resolved using specular reflectivity, in-plane diffraction, and rod scattering techniques. The combined scattering geometries provided important overlapping constraints to determine a single structural model. The combined structural model and kinetic observations accounts for the inconsistent structural studies in the literature.
Chapter 2

Background

Understanding the atomic surface processes and growth modes will aid in understanding growth of Pb films on the Si(111) surface and what motivates the interesting kinetic observations of the system. In this chapter we will highlight Pb-atom motions both individual and collective. Pb-film growth follows the Stranski-Krastinov (SK) growth mode, as opposed to two other types of growth, introduced here. As part of SK growth, Pb-islands form on the Si(111) surface after the initial wetting layer. However, Pb-islands on the Si(111) surface exhibit discrete height selection, at low temperature, and a simple particle in a box model is introduced to describe this observation. As a consequence of height selection, interesting island coarsening is observed. This coarsening is mitigated by the wetting layer between the nano-islands. Thus, previous attempts to determine the structure of the wetting layer are introduced, and the limitations of the final structural determination will be described.
2.1 Film Growth Modes

Figure 2.1: This figure shows different processes exhibited by adsorbed atoms on a surface [12]. The left half of the figure shows individual atomic processes. Atoms can diffuse across the surface, nucleate with other atoms, desorb from the surface, and diffuse into the substrate. The right side of the figure shows collective behavior of adsorbed atoms. Atoms can form a continuous layer, called a wetting layer. The distance between atoms in the wetting layer deviate from bulk bond-lengths, due to substrate interactions. Finally, atoms can form clusters with bulk bond-length atomic distances. The reduction of surface tension is driving force for wetting layer or bulk formation, and associated surface tensions are given for each situation.

Atoms adsorbed onto a substrate follow several different individual processes on the surface [12]. Individual atomic processes are shown in Fig. 2.1(a). The diffusion process involves an individual adsorbed atom hopping from one surface binding site to another and requires a minimum hopping energy \( E_D \). This means that an adsorbed atom travelling across a surface must hop from one site to another each time overcoming a minimum binding energy. Moreover, site hopping also depends on the temperature of the system, with increased temperature correlating with increased hopping rates. With enough energy, an atom can also leave the surface; once the desorbed atom leaves, it no longer interacts with the surface. Adsorbed atoms can form bonds with other atoms in a process called...
nucleation. Nucleation can be favorable if it minimizes total surface energy, but must also overcome a binding energy barrier ($E_B$). Adsorbed atoms in some systems may inter-diffuse into the substrate and form chemical bonds. However, the Pb/Si(111) system exhibits no inter diffusion and adsorbed Pb-atoms remain on the surface.

![Figure 2.2](image.png)

Figure 2.2: This figure shows three different growth modes for adsorbed atoms on a substrate [13]. Growth of over-layers is usually given in terms of coverage (ML) which corresponds to a single adatom per surface site. The first growth mode involves adatoms forming continuous layers on top of the surface, called Frank-Van der Merwe. Each layer is completed before the next layer begins to form. The second growth mode involves forming a single layer, called the wetting layer followed by growth of clusters on top of the wetting layer. This growth mode is called Stranski-Krastinov. The

Collective atomic growth also plays an important role in surface science which involve clusters, continuous films, or both. Models which describe film growth are based on minimization of surface energy. Collective behavior is driven by minimizing surface tension. Each interface and surface for adlayer and substrate has a surface/interface tensions indicated in Fig. 2.1. The bare substrate has an initial substrate-vacuum tension ($\gamma_{sv}$). Substrate surface reconstructions alleviate the substrate-vacuum tension when there are no adsorbed atoms on the surface. Adatom overlayer on the surface have two interfacial tensions from each side of the overlayer. The substrate-overlayer interface has an interfacial tension ($\gamma_{cs}$) which is likely to be lower than for the substrate-vacuum tension. The top of the overlayer at the overlayer-vacuum interface also has an interfacial tension ($\gamma_{cv}$). Minimization of the
surface and interface tensions strongly influence the type of overlayer structures that grow on the substrate.

Overlayer growth can follow one of three growth modes, shown in Fig. 2.2. Layer-by-Layer (Frank-van der Merwe) growth involves a continuous film growing on each completed film layer below. This means that a single layer completes before the next layer grows. Cluster growth (Volmer-Weber) involves adatoms forming bulk crystals on top of the substrate surface. No continuous film growth is involved in cluster growth. A final growth type (Stranski-Krastinov) involves both continuous film and cluster formation. In SK growth mode, the first layer forms a continuous film on top of the substrate, called the wetting layer. Coverage above the first layer involves cluster formation on top of the first continuous layer.

The Pb/Si(111) system follows the SK growth mode below room temperature. The first layer of Pb-atoms form a wetting layer on top of the substrate. After the first layer, bulk Pb-crystals begin to form. Above 10ML of Pb-coverage, the Pb-crystals coalesce and the surface begins layer-by-layer growth. However, unlike standard SK growth, Pb-crystals have discrete heights. Moreover, some island heights are preferred over others. The interesting deviations from SK growth, in the Pb/Si(111) system is still an ongoing interest in the surface science field.

### 2.2 Quantum Size Effects (QSE)

Pb islands grown on the Si(111)7x7 surface deviate from the SK growth mode because they exhibit flat tops and discrete heights. Figure 2.3 shows an STM image of Pb-islands grown on the Si(111)7x7 substrate at -45°C [2]. The wetting layer appears as a rough sur-
Figure 2.3: This figure shows the interesting discrete Pb-island height observations in the Pb/Si(111)7x7 system. The right image shows an STM image taken shortly after deposition of \( \sim 1.2 \text{ML} \) at -45°C [2]. The image clearly shows islands with flat tops and discrete heights. The island height for each island is labeled in units of bulk Pb-layers above the wetting layer. The left image shows a phase diagram of the island height temperature-coverage dependence [3]. The phase diagram was obtained by collecting STM images taken on the Pb/Si(111)7x7 surface for the given coverage deposited at the indicated surface temperature.

Further island height studies indicated that some heights were preferred in the system [3]. Moreover, the preferred height of the system changed with coverage and temperature. The phase diagram in Fig. 2.3 shows the interesting island height selection observed in the Pb/Si(111)7x7 system. The system shows regions where 5, 7, or 9 layer heights are preferred. Interestingly, the coverage boundary between a completed wetting layer and island growth shows a temperature dependence. Even the growth mode of the Pb/Si(111)7x7
system exhibits a temperature dependence. Above \(~270K\) the Pb/Si(111)7x7 system only exhibits bulk Pb(111) cluster formation. Whereas, below \(~230K\) the Pb/Si(111)7x7 system exhibits layer-by-layer growth above a certain coverage.

### 2.2.1 Particle in a Box Model of QSE

\[
\varepsilon_p = \frac{\hbar^2}{2m_p} \left(\frac{2\pi}{L}\right)^2 n_p^2
\]

\[
\varepsilon_z = \frac{\hbar^2}{2m_z} \left(\frac{\pi}{d}\right)^2 n_z^2
\]

Figure 2.4: shows a model for a QSE-island which is (a) sufficiently large parallel to a substrate to be subject to the Born-von Karman condition, but (b) is finite in the z-direction and therefore subject to particle in a box boundary conditions. The energy levels for each condition are given above the figures.

Discrete island formation can be understood by approximating the islands as cylindrical objects, with large in-plane width but small perpendicular height. The approximation is useful because it allows the electron density calculations to be separated into in-plane and perpendicular components. Figure 2.4(a) shows the cylindrical model approximation for a single island. In-plane, the islands are sufficiently large \((>100\text{nm})\) so that the Born Von-Karman periodic boundary condition can be applied. However, the perpendicular component of the islands makes the Born Von-Karman condition no longer valid. Consequently, the discrete heights can be modeled with a simple quantum mechanical particle in a box model, as shown in Fig. 2.4(b). With the particle in a box model the boundaries of the
islands are confined the the substrate-island interface and the island-vacuum interface. The electron confinement energy levels are strongly influenced by the size of the islands. Thus, the model predicts discrete heights which are multiples of the electron wavelength along the perpendicular direction.

Determining if the quantum mechanical particle in a box model can predict the observed Pb island heights requires comparing the the fermi-level electron wavelength for the discrete density of states with the observed island heights. The electron density for the particle in a box states are calculated [4, 5]:

\[
\rho(z) = \frac{1}{\pi d} \sum_{n=1}^{n_0} \frac{(k_f^2 - k_z^2) \sin^2(k,z)}{k_f^2 - k_z^2 \geq 0}
\]

or

\[
\Delta n_0 = \text{int} \left( \frac{k_fD}{\pi} \right) = \frac{\Delta N d}{\lambda_f/2}
\]

Here, the highest occupied band has a quantum number \(n_0\). Consequently, the change in the number of layers (\(\Delta N\)) must then satisfy the condition that the change in the maximum electron state (\(\Delta n_0 = 1\)) and maintain the particle in a box condition. Therefore, the allowed heights occur when the change in discrete island heights equals half the fermi-wavelength, for the highest occupied electron state of the new island height.

The allowed layer heights calculated for Pb(111) islands predicted an interesting bilayer film stability. Pb-films grow along the (111) direction on the Si(111) surface. Consequently, the Pb(111) fermi-wavelength, which effects the quantum well model, and associated fermi-energy level can be compared with the quantum well energy bands for Pb-films [5]. Where the two energy levels are coincident results in a stable island. Figure 2.5 shows
the single electron levels, filled to the bottom of the p-band at the L-point, compared with quantized energy levels per film layer. The fermi-wavelength is $\sim 0.44$ times the $\Gamma$-L zone length. Therefore, the allowed finite layer spacing allowed in this model are obtained by the expression: $\Delta N = \frac{d/0.44}{d} = 2.2ML$. Thus, the quantum well model predicts bi-layer stable heights in the Pb/Si QSE-system.

Photo-emission studies of uniform Pb-films support the quantum well model bi-layer stability prediction. Uniform films were grown on the Si(111)1x1 surface at low temperature to obtain electron binding energies [42], and determine if some layer heights are more stable than others. Figure 2.6 shows the binding energy of electrons as a function of Pb-film thickness. The figure clearly shows heights of 5, 7, and 9 layers give strong binding energy states. The photo-emission heights match the bi-layer stability of the quantum well model. Furthermore, the preferred film thicknesses correspond with the equilibrium heights observed in STM studies in Fig. 2.2 [3]. Thus, the simple quantum well assumption provides
Figure 2.6: This figure shows observed photo-emission binding energy states vs. Pb-film thickness. The figure is reproduced from Up- 
ton et. al [42]. The surface was prepared by growing uniform Pb- 
films on the Pb/Si(111)1x1 sur- 
face at 100K. Quantum well en-
ergies are observed at 5,7,9 ML 
thickness. The quantum well en-
ergies correlate with the theoret-
ically calculated bi-layer stabil-
ity [5], and STM observed island 
heights [3]

an effective model to explain quantized Pb island heights grown on the Si(111) surface.

The correspondence between photo-emission and initial STM studies is also surprising since they were performed on different surface structures. The photo-emission studies were performed with Pb films grown on the Si(111)1x1 surface. Whereas, initial STM analysis was performed on the Si(111)7x7 surface. The quantum well model initially considered the walls of the well to be of infinite potential. Thus the experimental results suggests that the Pb islands do not significantly interact with the Si(111) surface below. This is further complicated because Pb islands sit on top of the bare Si(111)7x7 substrate and not the wetting layer as initially assumed [27].

2.2.2 Non-preferred Island Growth and Coarsening

Interestingly, heights which are not predicted by the quantum well model are still observed in the system. Figure 2.3 shows islands with a distribution of discrete layers. The 3,4,6 island heights which are not predicted by the model, while the 5,7 layers are predicted. How-
Figure 2.7: This figure shows coarsening behavior for Pb-islands grown on the Pb/Si(111)7x7 surface using both STM and X-ray diffraction. The image is reproduced from C.A. Jeffrey et al. [27]. The fractional area of the substrate covered by islands vs. island height was studied using STM analysis for 1.6ML Pb grown at -45°C. The Pb-atoms were deposited using a \((a)\) fast deposition rate (0.5ML/min) and a \((b)\) slow deposition rate (0.05ML/min). The islands were observed just after deposition ~5min and 74min after deposition. \((c)\) X-ray studies of the island density show that higher flux rates lead to faster decay times. The relaxation rate \((\tau)\) and initial island density \((n_0)\) are plotted vs. flux rate as insets.

However, studying the time-evolution of island coverage shows that islands with non-preferred heights decay. Figure 2.7(a,b) shows the observed decay as a function of time for two different deposition rates. Fast deposition of Pb creates a large number of non-preferred islands, which quickly decay. Interestingly, depositing Pb at a slower rate creates non-preferred 4ML islands, which remain on the surface. Slower deposition rates create islands which cover more surface area per island, and therefore it takes longer for larger unstable islands to decay. Importantly, this shows that the coarsening process of Pb-islands has an extra contribution from the unstable island decay.

Island coarsening on the Pb/Si(111)7x7 surface was initially expected to follow a classi-
cal power law behavior, as described in eqn. 2.2. The equation describes the time dependent island density, with an initial island density \( n_0 \) and time constant \( \tau \). The exponent \( \beta \) is dependent on the dimensionality of the system \( m \). Importantly, island density for long times \( \left(t \gg \tau\right) \) is independent of the initial island density, \( n \propto t^{-\beta} \). Therefore, island decay in the Pb/Si(111)7x7 system should exhibit the same long time behavior classical coarsening predicts.

\[
n(t) = n_0(1 + \frac{t}{\tau})^{-\beta}
\]  
\[
\beta = \frac{2}{(m + 2)}
\]  
\[
m = 0, 1, 2
\]

X-ray diffraction studies of Pb-island coarsening showed a surprising deviation from classical coarsening behavior [27]. Figure 2.7(c) shows the observed Pb-island coarsening on the Si(111)7x7 surface at -45°C. The island density does follow a power law behavior on the surface. However, none of the island density curves converge over long times. Furthermore, the time constant \( \tau \) is orders of magnitude larger than expected, based on observations of larger Pb-crystals [6, 7]. Correlating the deviation from classical coarsening with the STM observations, in fig. 2.7(a), suggests that non-preferred islands initially grow but are unstable and quickly decay leading to the fast coarsening observations.

The fast coarsening time and unstable island decay is mitigated fast mass transport across the wetting layer, from unstable islands to stable islands on the surface. The mass transport is surprising when considering to the individual atom diffusion processes described in fig. 2.1. Individual atoms must detach from the top of unstable islands and
diffuse down island, as seen on the right half of the figure. Also, atoms must diffuse across the surface toward other stable islands. However, the SK growth of the Pb/Si(111)7x7 system requires that atoms diffuse across the wetting layer and not the substrate, as indicated in fig. 2.2. This diffusion process across the wetting layer is then further complicated when considering the structure of the wetting layer.

2.3 Wetting Layer Phases

The Pb/Si(111)7x7 interface has a complicated temperature and coverage dependence, which has been explored extensively using STM and X-ray scattering [19, 20, 10, 8, 9]. The different techniques have lead to conflicting structural models for the low temperature wetting layer. The presence of Pb atoms negate the need for the 7x7 reconstruction, and annealing the Pb/Si(111)7x7 surface results in a complicated collection of different Pb/Si(111)1x1 surface structures [37]. Reviewing the Pb/Si(111) structures is useful background for understanding the structures investigated in this dissertation.
2.3.1 Si(111)7x7 interface

Figure 2.8: This figure shows the in-plane and vertical Si atom positions in the 7x7 unit cell. The atomic layers are named: layer-1b which is the bottom layer closest to the Bulk Si(111), layer-1a as the next layer above layer-1b, and adatoms are the top-most layer above the bulk [18]. A completely occupied bulk 7x7 unit cell would have 49 atoms. Layer-1b has 48 Si atoms occupying bulk Si(111) lattice T4 sites. Layer-1a has 42 Si atoms occupying T1 sites. The adatom layer has 12 Si atoms occupying T4 sites, above layer-1b. The 7x7 unit cell has an extra mirror symmetry line from cutting the cell into two halves (faulted/unfaulted). The mirror line, shown as a thick solid line, cuts the in-plane unit cell area into two triangles, in the in-plane diagram. The unfaulted half continues the ABC diamond stacking of the substrate. Unlike the faulted half, which breaks the stacking sequence, which masks the bulk layers preventing them from being seen below the 7x7 surface in in-plane. The 7x7 exhibits and extra level of symmetry within the unit cell, called pseudo-symmetry. The pseudo-symmetric sub-unit cell is given as a triangle with a dashed outline, and reproduces the rest of the 7x7 unit cell under symmetry operations.
The Si(111)7x7 surface has a complicated multi-layer reconstruction driven by the minimization of dangling bonds at the surface. Figure 2.8 shows the top three reconstructed layers of the surface. The lowest layer, called layer-1b, has 48 atoms with Si-atoms. Interestingly, the Si atoms along the sides of the unit cell, in layer-1b, form dimer pairs. Atoms in layer-1b occupy sites designated as T4-sites on the hexagonal lattice. The next layer, called layer-1a, has 42 atoms which form triangular sub-units with layer-1b. The top layer, called the adatom layer, has 12 atoms sitting above layer-1a positions. Atoms in layer-1a occupy sites designated as T1-sites on the hexagonal lattice. The unit cell follows six-fold (p6mm) symmetry in-plane, unlike the three-fold (p3m1) symmetry of bulk Si(111), which is indicated by the hexagon at the origin of the in-plane unit cell diagram. The extra mirror plane splits the unit cell into faulted and unfaulted halves. The unfaulted half of the unit cell continues the stacking sequence of Si(111), whereas the unfaulted half of the unit cell breaks the stacking sequence. The clean Si(111)7x7 unit cell provides the foundation for subsequent Pb/Si(111) interface structures.
2.3.2 Previous Pb/Si(111)7x7 structural models

Figure 2.9: STM studies have suggested different coverage dependent Pb/Si(111)7x7 structures. The initial three Pb atoms occupy Si 7x7 sites on the faulted half of the unit cell [19, 20]. The next three Pb atoms fill the equivalent mirror symmetry sites on the unfaulted half of the unit cell. Beyond the initial six sites, Pb atoms begin to randomly occupy the remaining T1 sites on the surface, possibly displacing with Si adatoms, which moved to other random surface sites [20]. At ~1ML, Pb atoms occupy all the T1 sites on the surface, and also form dimer pairs along the edges of the unit cell [10].

STM studies on the Pb/Si(111)7x7 surface at 30°C show Pb atoms initially follow the Si(111)7x7 symmetry [19, 20, 10]. Figure 2.9 shows the coverage dependent structures proposed, based on STM observations. The first three Pb atoms (at 0.06ML) occupy T1 sites between Si adatoms on the faulted half of the unit cell. The addition of three more Pb
atoms (at 0.12ML) fills the equivalent mirror symmetry positions on the unfaulted half of the unit cell. Between 0.12ML and 0.6 ML, Pb begins to displace Si adatoms on the surface, occupying T1-sites directly above Si layer-1a positions. It was proposed that Si adatoms are displaced randomly to other sites on the surface. Around 1ML Pb-atoms occupy most of the T1-sites above layer-1a, as well as form dimer pairs near the unit cell edges [10].

There were several limitations of the STM studies which prevented a complete structural determination. STM is only sensitive to the top most layer on the surface; consequently, the height of the Pb atoms, above the Si surface, was not distinguishable in the studies. Furthermore, displacements of Si atoms below the Pb layers was not observable. In-plane atomic resolution was prevented Pb atom position determination to less than 4-5Å. Finally, the surface preparation for the 1ML studies involved deposition at ~30°C followed by an anneal above ~150°C, quench back to ~30°C, and further deposition. The three-step preparation technique created a different surface than the single step process would. Furthermore, the authors noted multiple disordered structures on the surface.
Figure 2.10: This figure shows the model proposed by X-ray diffraction studies done on the Pb/Si(111)7x7 surface [8, 9]. The Pb-atoms occupy an 8x8 lattice commensurate with the Si(111)7x7 unit cell. The 8x8 lattice follows the six-fold symmetry of the substrate. This model produces strong in-plane X-ray diffraction intensity at $8^*\left(\frac{a}{7}, \frac{m}{7}\right)$.

The Pb/Si(111)7x7 surface was also studied using in-plane X-ray diffraction resulting in a proposed 8x8 lattice model commensurate with the 7x7 unit cell [8, 9]. Figure 2.10 shows the structure the 8x8 commensurate Pb layer above the Si(111)7x7 surface. The lattice follows the six-fold symmetry of the 7x7. Also, the 8x8 lattice follows the pseudo-symmetry of the 7x7 unit cell. The bond length for the Pb atoms within the 8x8 is 3.36Å, which is shorter than the hexagonal in-plane bulk Pb-Pb bond length of 3.5Å. The in-plane diffraction analysis suggested the Pb atoms were strained from the ideal 8x8 sites within the structure. However, due to a limited data set, a complete structural determination was not possible. Furthermore, the study was performed with 2.5ML Pb-coverage, and Pb-islands form above 1.0ML which consume the wetting layer and may have contributed limitations in structural determination.
2.3.3 Pb Structures On Si(111)1x1

Annealing the Pb/Si(111)7x7 surface above 200°C transforms the surface to a Pb/Si(111)1x1. The existence of a metal on the Si(111) surface negates the need for the 7x7-reconstruction, therefore, causing the transformation to the 1x1 surface. Consequently, this transition is irreversible. Upon cooling the Pb/Si(111)1x1 surface, a complex collection of coverage-dependent structures form. Several phase diagrams have been proposed for Pb on the Si(111)1x1 surface [36, 37, 39]. Figure 2.11(a) shows a phase diagram of the cover-
age/temperature dependent surface determined using STM/SPA-LEED analysis. The Pb phases on the Si(111)1x1 surface are interesting because QSE nano-islands have also been observed with these phases [38]. Whereas recent real-space analysis studies indicate that the Pb phases are commensurate with the Si(111)1x1 surface [37, 38]. However, early diffraction studies [8, 9, 23] indicated possible incommensurate structures, as will be discussed in the next section.

Two examples of Pb structures, shown in fig. 2.11(b,c), provide a basis for the complicated domains that exist on the Si(111)1x1 surface. Interestingly, multiple Pb structures exist simultaneously on the Si(111)1x1 surface, because they are very close in energy. One of these domains (not shown in the figure) is called the "devils staircase" phase. The basis for the devils staircase phase are the $\sqrt{7}x\sqrt{3}$ and $\sqrt{3}x\sqrt{3}$ structures. A SPA-LEED analysis showed that these two structures exist at the same time between $\sim0.9$ and $\sim1.2$ML [39]. Below $\sim0.9$ML and 30°C, the $\sqrt{7}x\sqrt{3}$ phase is dominant on the surface. Importantly, the latter coverage-dependent determination will affect observed X-ray diffraction analysis, described in the next section.
Figure 2.12: shows X-ray diffraction data taken from Grey et al. [8, 9] on the Pb-phase. The radial scan (upper Left) of the (2/3,2/3)H diffraction spot was taken on the surface with 2.2ML of Pb-coverage. A transverse scan (upper Right) of the second peak in the radial scan showed two symmetrically spaced spots. A figure of the α-phase (lower left) showing the position of the peaks and a close-up (lower right) shows the symmetries of the peak positions.

X-ray scattering studies on the $\sqrt{3} \times \sqrt{3}$ phase, also called the α-phase, on the Si(111)1x1 surface, which exists above $\sim$1.2ML [8, 9]. They prepared the α-phase by annealing a $\sim$2ML Pb/Si(111)7x7 surface to 200°C, followed by a quench to 30°C. Figure 2.12(a-d) shows the observed grazing incidence X-ray diffraction near the $(\frac{2}{3}, \frac{2}{3})$. Along with a single diffraction peak near the (0.65, 0.65) position, two satellite peaks were also observed, which are associated with domain walls which form with incommensurate surface structures. The
location of the Bragg peak, combined with satellite locations, led to the conclusion that the \( \alpha \)-phase was incommensurate with the Si(111)1x1 substrate. A later electron diffraction study also confirmed the observation of satellite peaks [23]. Consequently, the interpretation of the observed satellite peaks has been left unresolved. This dissertation will address the observed satellite peaks with the \( \alpha \)-phase, and show that they correspond with bulk Pb crystals rather than domain walls.
Chapter 3

Scattering Techniques and Theory

3.1 Scattering Geometry

X-ray scattering can reduce a complex three-dimensional scattering process down to one or two-dimensional observations depending on the geometry of scattering. For example, in-plane diffraction studies atomic order in two dimensions when the beam grazes the surface of the crystal. The scattering geometry can be determined by the orientation of the sample and detector, as shown in Fig. 3.1. The incoming X-ray beam \( k_i \) is described by in-plane \( (\phi_i) \) and out-of-plane \( (\theta_i) \) angles. The scattered beam \( k_f \) is also described by in-plane \( (\phi_f) \) and out-of-plane \( (\theta_f) \) angles. These in-plane and out-of-plane angles determine what range of the sample is being probed X-rays.

\[
Q \equiv k_f - k_i
\]  

(3.1)

The process of elastic X-ray scattering involves a wave vector transfer from the sample
on the scattered beam. Describing this wave vector transfer is done by using the momentum
transfer vector (Q), as shown in Fig. 3.1. Like the scattering vectors, the momentum trans-
fer vector has both in-plane (Q∥) and out-of-plane (Q⊥) components, and is related to the
scattering vectors given by eqn. 3.1. Here we will consider different scattering processes
described by eqn. 3.1 and used in the structural analysis of Pb/Si(111)7x7 interface.

Figure 3.1: This figure shows the general scattering geometry for X-ray scattering ex-
periments. The sample space geometry has coordinates (x,y) defining the sample surface
plane, and z-axis defining perpendicular to the surface plane. The incoming beam k₁ has
both in-plane (φ₁) and out-of-plane (θ₁) angles. The outgoing beam k₂ also has in-plane
(φ₂) and out-of-plane (θ₂) angles. The two vectors define the momentum transfer vector
[Q(Q∥, Q⊥)]. The momentum transfer vector defines a sphere of allowed scattering condi-
tions, called the Ewald sphere.
3.2 Reciprocal Lattice and Intensity

Figure 3.2: This figure shows the relationship between the vectors which describe real-space atomic positions and vectors which describe reciprocal space positions of Bragg diffraction. The figure shows a surface of two-planes of atoms in a cubic lattice. The real-space atomic positions are described by the atomic vector ($\vec{R}_i$) and basis vectors ($\vec{a}_1, \vec{a}_2, \vec{a}_3$). The incoming and outgoing wave vectors describe the reciprocal space vector ($Q$) with basis vectors ($\vec{b}_1, \vec{b}_2, \vec{b}_3$). The two sets of basis vectors are related by eqn. 3.2.

Calculating wave vectors, which lead to constructive interference, depend on the real-space structure, as shown in Fig. 3.2. Each atom ($\vec{R}_i$) in the sample is determined using unit vectors ($\vec{a}_1, \vec{a}_2, \vec{a}_3$) in real space. The momentum transfer vector ($Q$) positions, which describes positions of constructive interference, are given by integer values (H,K,L) in reciprocal
space. The reciprocal space vectors are related to the real-space vectors through eqn.3.2. Therefore, the reciprocal-space integers (H,K,L) are determined directly from the atomic positions in real-space.

\[
\begin{align*}
\vec{Q} \cdot \vec{a}_1 & \equiv 2\pi H \\
\vec{Q} \cdot \vec{a}_2 & \equiv 2\pi K \\
\vec{Q} \cdot \vec{a}_3 & \equiv 2\pi L
\end{align*}
\]

The observed quantity in an x-ray scattering experiment is the intensity (I) of the scattered wave, which can vary depending on the structure. Crystals can have multiple types of atomic elements, with different electron densities, in many different arrangements. The complexity of the crystal results in different scattered intensity for different reciprocal-space integers (H,K,L). The structure factor (F), defined in eqn. 3.3 uses reciprocal space to account for the scattered wave from each atom in the crystal. The structure factor is a complex number which sums the electron density (f(q)) for each atom in the crystal multiplied by the Fourier components of the scattered wave. Because the structure factor is complex, it has both an amplitude and phase. The observed intensity of the scattered wave is then directly related to the structure factor, as shown in eqn. 3.4. Therefore, the observed intensity in an experiment can be explained by calculating the structure factor of a model surface.

\[
F(\vec{Q}) = \sum_{j=1}^{N} |f(\vec{Q})|e^{i(\vec{Q} \cdot \vec{R}_j)} = |F(\vec{Q})|e^{i\alpha(\vec{Q})}
\]

In the second part of eqn. 3.3, the complex structure factor is represented, separately, by its real and complex components. The real component of the structure factor (|F|) describes
the amplitude of the scattered wave, while the complex component of the structure factor \( \alpha(\vec{Q}) \) describes the phase of the scattered wave.

\[
I(\vec{Q}) \propto |A_0 \frac{e^2}{mc^2} \frac{1}{R_0} F(\vec{Q})|^2
\]

(3.4)

Scattered intensity observed for a crystal is proportional to the square modulus of the structure factor. The scattered intensity is also related to the amplitude of the incoming beam \( (A_0) \), distance from sample to detector \( (R_0) \), and constant \( (\frac{e^2}{mc^2}) \). The square modulus of the complex structure factor function results in a real function of \( \vec{Q} \), without any phase information. This is known as the phase problem of X-ray scattering.

### 3.2.1 Reflectivity

Specular reflectivity geometry involves considering only out-of-plane scattering, with the incoming and out-going waves having the same angle with the surface \( (\theta) \). Figure 3.3(a) shows the simplified real-space geometry, with each vertical layer of atoms extending to infinity. In this geometry the reciprocal lattice integers \( (H,K) \) are zero. First, we can ignore the surface components and only consider the bulk crystal. With this assumption, the summation of all atoms in the bulk structure is then a geometric sum of infinite terms:

\[
F(\vec{Q}) = \sum_{j=1}^{\infty} |f(\vec{Q})| e^{i(\vec{Q}\cdot\vec{R}_j)} = \frac{1}{1 - e^{-i(2\pi L)}}
\]

\[
I(\vec{Q}) \propto |I_0 F(\vec{Q})|^2 = [I_0]^2 \frac{1}{sin^2(\pi L)}
\]

(3.5)
Figure 3.3: This figure shows a simple cubic structure with a possible surface reconstruction. The real-space structure shows a bulk substrate with a bulk inter-planer spacing, d. The surface has a single reconstructed layer with vertical lattice constant (a). The positions for each atom can be added to an effective $-\infty$ with the surface layer as origin. Specular reflectivity is insensitive to in-plane motion, but can observe changes in atomic density and vertical position. The specular reflectivity intensity for this real space model is shown as a function of perpendicular reciprocal lattice unit (L). The solid curve shows specular reflectivity for an ideally-terminated cubic substrate. The dashed curve shows reflectivity if the top surface layer were shifted 20% farther from the substrate. The dotted curve shows reflectivity if the top layer had the bulk-lattice constant (d) but 80% of the bulk atomic density.

The scattered intensity, for this simple assumption, results in integer values of L, as shown by the solid line in Fig. 3.3(b). Where the scale factor $I_0 = A_0 \frac{e^2}{mc^2} \frac{1}{R_0}$. Thus, the scattered intensity becomes infinite for integer values of L. This simple calculation for the
scattered intensity of from a crystal, can be modified to include surface layers, which results in observed intensity between integer L-values. Intensity must also instrumental and geometrical effects which modify real scattering from a crystal; these geometrical effects will be described in the next chapter. Here, we will focus on the structure factor contributions.

The surface of any crystal may have one or more layers deviating from the bulk density and height values, such at the red layer in Fig. 3.3(a). The deviation will change the observed reflectivity intensity on the crystal, by changing intensity between Bragg points. However, in-plane atomic deviations of the surface layers are not observed in reflectivity, because the in-plane component of the scattering is zero. Consequently, the in-plane motions of the red-atoms in Fig. 3.3(a) will not be observed. Therefore, the geometry of reflectivity reduces the number of measurable parameters for each surface layer to a density \( \rho \) and height \( a \).

Equation 3.6 shows the structure factor for both surface and bulk terms of the cubic crystal in Fig. 3.3(a). The surface term has density parameter \( \rho \) referenced to the bulk. Thus, a density of unity is the same as bulk atomic layer density. Whereas, the height parameter \( a \) is given in units of distance, not referenced to the bulk lattice spacing \( d \). Using this model scheme, the structure factor could be easily modified to include more layers for any complicated structure which may involve multiple layers on the surface. By taking the square modulus of the structure factor in eqn. 3.6, as was done in eqn. 3.5, the experimentally observed intensity of any surface can be modeled.

\[
F(\vec{q}) = F_{bulk} + F_{Surface} = \frac{1}{1 - e^{-i(2\pi L)}} + \rho \cdot e^{-i(2\pi La/d)} \tag{3.6}
\]

Understanding the intensity profile for the toy surface illuminates how real surface structures are modeled using experimentally observed intensity. Figure 3.3(b) shows in-
tensity calculated with eqn. 3.6 for different modifications to the single surface layer. If the surface layer simply continued the density and lattice spacing of the bulk, then the observed intensity would create the solid line observed in the figure. The effects for each parameter cumulatively combine in a real structure, thus it is useful to understand each effect separately.

If the surface layer maintained the bulk density, but obtained a vertical shift were included, then the intensity would create oscillations between the Bragg peaks. Figure 3.3(b) shows a layer shift away from the bulk by \( \sim 20\% \), resulting in the oscillation observed in the intensity (line-with-square). The increased distance corresponds with a shift of the lowest point in the intensity from \( L=0.5 \) r.l.u. to \( L=0.4 \) r.l.u., and the effect becomes further distinguished with increasing \( L \). Alternatively, if the top layer distance from the bulk were decreased by \( \sim 20\% \), then the opposite behavior would be observed, where the lowest intensity would shift toward \( L=0.6 \). Importantly, the beating oscillation between the surface layer and bulk terms results in sharp cusp behavior near the Bragg points. The model intensity shows a strong cusp on the high side of the \( L=2.0 \) Bragg point. These sharp cusps are sensitive to small perturbations in the parameter and provide excellent constraints for modeling experimental data.

The second deviation of the model surface layer involves keeping the bulk layer height maintained, while modifying the layer density. Figure 3.3(b) shows a layer density reduction by \( \sim 20\% \), resulting in the strong dips observed in the intensity (dashed-line). Unlike the layer height, changing the bulk density does not shift the location of lowest intensity. Instead, reducing the density creates a beating pattern which lower the intensity at \( L=5 \) while increasing the intensity near the Bragg points. Decreasing the density corresponds with missing atoms in the layer, as in the toy model shown in Fig. 3.3(a), for
homogeneous-epitaxial systems. However, the density parameter becomes more complicated for hetero-epitaxial systems where the adatoms on the surface have different atomic scattering power than the substrate. Thus, a changing density can have contributions from total number of atoms as well as scattering power per atom.

3.2.2 In-plane Diffraction

The second scattering geometry involves only in-plane momentum transfer, called grazing incidence geometry. We also consider the restriction where the in-coming and out-going wave vectors have the same in-plane angle ($\phi$). With this restriction, Bragg peaks occur in grazing incidence diffraction from in-plane two-dimensional atomic order on the surface. In-plane diffraction matches surface symmetries of the crystal structure: for example, cubic crystals can take on four-fold symmetry in-plane which would result in a diffraction map which is also four-fold symmetric. This relationship is advantageous, because minor deviations from the crystal symmetry would be observed in diffraction data. Therefore, in-plane diffraction is sensitive to various deviations in atomic order, such as atomic strains or defects on the surface.

In-plane diffraction cannot distinguish vertical displacements for different atomic positions, because there is no out-of-plane momentum transfer. This means that complicated multi-layer reconstructions will be observed as a single layer with in-plane diffraction. As previously described, specular reflectivity is insensitive to in-plane atomic motions but can distinguish vertical displacements. Also, reflectivity can distinguish average atomic densities of complicated surface reconstructions. Therefore, in-plane diffraction and reflectivity are indirectly related through the average density of each layer. In-plane atoms can be assigned heights by relating the number of atoms to atomic density in a layer.
Figure 3.4: This figure shows the relationship between real space interface structures and reciprocal space in-plane diffraction. (a) The outlined shaded box shows a simple cubic interface with a single reconstructed surface layer with four atoms per unit cell, which is a larger unit cell than the substrate. The in-plane symmetry follows a four-fold rotation axis, perpendicular to the surface. (b) A top view of a single 4x4 unit cell shows the surface atoms take on an in-plane strain. The ideal lattice positions are indicated by shaded circles with dashed outlines. The strained positions are indicated by solid circles with arrows indicating direction of strain. The pseudo-symmetric sub-unit cell, outlined by the dashed mirror lines, indicates extra surface symmetry within the unit cell. (c) If the surface atoms exhibit a 5% strain, then the resulting in-plane diffraction pattern shows intensity at quarter integer positions. The map shows only positive H-values with both positive and negative K-values, highlighting the four-fold surface symmetry. Mirror symmetry lines are indicated as solid lines. The pseudo-symmetry of the unit cell can be determined in the diffraction pattern, as indicated by the dashed lines.
Consider now the same simple cubic crystal from reflectivity, but with a surface reconstruction that has a surface atom ever other bulk site, as shown in Fig. 3.4(a). The unit cell has four surface atoms for every 16 bulk atoms in a unit cell. However the four surface atoms can take on an in-plane strain directing each atom toward the center. A useful top view of a single unit cell is shown in Fig. 3.4(b). This surface reconstruction creates a larger unit cell which has four times the length of the bulk atomic distance, as is indicated in the shaded boxes on the surface. The larger unit cell maintains four-fold symmetry in-plane. Thus, rotating about the origin every 90° results in the exact same observation. In general the allowed crystal symmetries are 1,2,3,4,6 for any surface [25, 26]

**Structure Factor of Cubic Surface**

The structure factor calculation of the in-plane diffraction model of Fig. 3.4 is calculated as:

\[ F_{\text{cube, tot}} = F_{\text{cube, bulk}} + F_{\text{cube, rec}} \]  

\[ F_{\text{cube, rec}} = \rho e^{i2\pi(H+K)(1+\epsilon)} + \rho e^{i2\pi[3H+K+\epsilon(K-H)]} \]

\[ + \rho e^{i2\pi[H+3K+\epsilon(H-K)]} + \rho e^{i2\pi[3H+K-\epsilon(H+K)]} \]

There are four atoms in the structure, with single atomic density parameter (\(\rho\)), as well as a single in-plane strain parameter (\(\epsilon\)). The strain parameter forces all every surface atom to move the same distance toward the center of the unit cell. The parameters chosen for this model were \(\rho=1.0\) and \(\epsilon=0.01\), corresponding with surface atoms having bulk density and a 1% strain toward the unit cell center. These parameters were used to create the diffraction map in Fig. 3.4(c).
Cubic Model Diffraction Map

The in-plane diffraction map for the cubic model of eqn. 3.7, presented in Fig. 3.4(c), highlights the important features in surface diffraction. The integer order spots are referenced to the bulk lattice constant \(a_c\), defined as unity. Because the diffraction map is referenced to bulk units, fractional spots will be observed when the distance between atoms on the surface increases. Therefore, the number of peaks is directly related to the size of the unit cell on the surface, so that the 4x4 unit cell model is related to the \((\frac{n}{4}, \frac{m}{4})\) observed diffraction map. Mirror planes occur when diffraction intensities are equivalent under symmetry operations. However, determining mirror planes in experimental data can be complicated by strain in the surface. Initially, the bulk symmetry plans can be used with surface diffraction. But, surfaces can obtain greater in-plane rotational symmetry than bulk crystals, and further trial and error analysis may be required.

Pseudo-symmetry

The surface can also have symmetry operations within the unit cell, called pseudo-symmetry operations, which further simplify structural determination. In real-space, pseudo-symmetry operations can reduce a large surface unit cell down to a minimal sub-unit cell. The shaded triangle in Fig. 3.4(b) represents the pseudo-symmetric sub-unit cell of the larger 4x4 unit cell. The pseudo-symmetry mirror lines are indicated as dashed lines within the unit cell. Applying the dashed mirror line operations to the sub-unit cell can thus recreate the entire unit cell. For this simple cubic model every surface atom has the same strain and density parameter which makes the pseudo-symmetry reduction unnecessary. However, a complicated hetero-epitaxial surface can have multiple types of atoms and strain parameters which are difficult to model. Therefore, the larger unit cell model can be reduced to a minimal
parameter model of the surface.

The sub-unit cell, for the cubic model of Fig. 3.4(b), can then reduce the total unit cell structure factor calculation to a single atom structure factor. Equation 3.8 shows the sub-unit cell structure factor along with all the pseudo-symmetry operations to create the total unit cell. This sub-unit cell structure factor has the first atom of the total unit cell as a function \( F_{\text{sub}}(H',K') \). Importantly, the sub-unit cell has an extra factor \( \frac{1}{2} \) which corrects for double counting, because any atom that lays along a mirror line will always be double counted under symmetry operations. All of the pseudo-symmetry operations applied to the sub-unit cell are also given in eqn. 3.8(b). The pseudo-symmetry operations work by using the origin as the center of every mirror plane, which is the definition of point symmetry for a unit cell origin in crystals. Consequently, adding a translational phase factor for each symmetry operation results in reproducing the entire surface unit cell. For example, the phase \( e^{i\frac{2\pi}{4}H} \) is added to the symmetry operations \( [F_{\text{sub}}(-H, K) + F_{\text{sub}}(K, -H)] \) to reproduce the atom in the lower right corner of the unit cell of fig. 3.4(b).

\[
F_{\text{sub}}(H', K') = \frac{1}{2} \rho_2 e^{i\frac{2\pi}{4}(H'+K')(1+\epsilon)} \tag{3.8}
\]

\[
F_{\text{cube,rec}} = F_{\text{sub}}(H, K) + F_{\text{sub}}(K, H) + [F_{\text{sub}}(-H, K) + F_{\text{sub}}(K, -H)]e^{i\frac{2\pi}{4}H} + [F_{\text{sub}}(H, -K) + F_{\text{sub}}(-K, H)]e^{i\frac{2\pi}{4}K} + [F_{\text{sub}}(-H, -K) + F_{\text{sub}}(-K, -H)]e^{i\frac{2\pi}{4}(H+K)} \tag{b}
\]

The pseudo-symmetry mirror planes can be utilized with experimental diffraction data.
to simplify structural analysis. The pseudo-symmetry mirror planes for the cubic model are indicated by dashed lines on the diffraction map in Fig. 3.4(c). Averaging the diffraction peaks on either side of the pseudo-symmetry lines results in a minimal diffraction set, which can be seen as the highlighted triangle in the figure. Because the cubic model does not have any complicated symmetry violations, the data already follows the pseudo-symmetry operations. However, the model provides an instructive example about how to apply pseudo-symmetry. More complicated surface structures may not strictly follow surface symmetry, which makes structural analysis more difficult. By averaging the diffraction data about pseudo-symmetry mirror planes, the symmetry breaking modifications to the real structure can be averaged and simplified. Once the simplified model has been determined, the pseudo-symmetry restrictions can then be relaxed to obtain a more accurate structural model.

3.2.3 Bulk/Fractional Surface Truncation Rods

Including out-of-plane momentum transfer for the observed in-plane diffraction peaks provides vertical height information for in-plane atomic positions. Fractional in-plane diffraction peaks have continuous out-of-plane scattering components, because only a limited number of atoms contributing to the scattering. Consequently, scattering along continuous fractional peaks are called *fractional rods*. Because fractional rod scattering only includes the reconstructed surface layer atoms, fractional rod scattering provides information about how surface atoms are vertically ordered relative to each other. Alternatively, bulk in-plane diffraction peaks combine the surface layers contributions with the sharp Bragg scattering from the bulk. Thus, scattering along bulk diffraction peaks are called *bulk rods*. Consequently, bulk rod scattering provides vertical height information about surface atoms.
relative to the bulk substrate. However, any surface atom that does not coincide with a bulk lattice site will not be observed in bulk rod scattering. Therefore, combining both fractional and bulk rods the vertical heights of surface atoms can be determined. Furthermore, rod scattering provides a direct connection between surface layer heights determined by specular reflectivity and in-plane atomic order determined by in-plane diffraction.

Figure 3.5: This figure shows bulk and fractional scattering rods for the simple cubic structure from Fig.3.4. The modeled intensity is shown as a function of perpendicular rlu (L) and the symmetry equivalent rod is plotted with negative rlu. The bulk rods (1,0)(0,1) and fractional rods \((\frac{1}{2}, \frac{1}{2})(-\frac{1}{2}, -\frac{1}{2})\) extend from the in-plane diffraction positions in Fig. 4.3 with the same in-plane atomic strain. Diffraction rods can distinguish when the surface layer has the bulk vertical height (solid line) or a 20% shift away from the substrate (dashed lines). Rod scattering can also distinguish atomic density differences (dotted line) which can result from heterogeneous surface adsorption.
**Simple Cubic Structure Factor For Rod Scattering**

The cubic toy model provides an example for how the structure factor calculations for rod scattering combine the in-plane structure factors, from in-plane diffraction calculations, with the vertical structure factors, from specular reflectivity. The combined in-plane and vertical structure factor for the cubic model is given in eqn. 3.9. The in-plane structure factor for the reconstructed surface layer, from eqn. 3.7, is combined with the vertical structure factor for that layer from reflectivity, from eqn. 3.6. The bulk in-plane structure factor includes the 16 bulk atoms per 4x4 unit cell, as shown in Fig. 3.4(b), with the vertical bulk scattering term in eqn. 3.5. Thus, the scattering intensity for every fractional and bulk rod can be modeled with the combined structure factor.

\[
F_{\text{cube,rod}} = F_{\text{cube,rec}}(H, K, \rho, \epsilon)e^{i2\pi L a/d} + F_{\text{cube,bulk}}(H, K)F_{\text{bulk}}(L)
\]  
(3.9)

**Rod Scattering For Cubic Model**

The bulk and fractional diffraction rods from the cubic surface, calculated from eqn. 3.7, highlight the main advantages of using rod scattering for structural determination. Figure 3.5 shows rod scattering for both bulk and fractional rods, along with symmetry equivalent diffraction conditions. The rods are calculated for several possible conditions of the surface layer model parameters \((\rho, \epsilon, a)\). The symmetry equivalent rods are plotted along the negative L-axis, with the dashed line at origin indicating the mirror symmetry of the surface. Because, in-plane atomic positions can violate the strict pseudo-symmetry of the surface, plotting the symmetry equivalent scattering rods provides evidence of symmetry.
breaking on the surface which in-plane diffraction may not observe. Therefore, rod scattering is sensitive to both atomic shifts as well as any deviation from originally assumed surface symmetry.

Bulk rod scattering provides information about how surface atoms are ordered with substrate positions. When surface atoms sit near bulk sites, they interfere with the substrate and can be observed. Whereas, atoms that are not near bulk sites cannot be observed in bulk rod scattering. The initial surface model involves the four atoms at their strained positions ($\epsilon \sim 0.1$) with the bulk vertical height and atomic density. Figure 3.5 shows the bulk (1,0)(0,1) rods for the initial model (solid line). Shifting the surface layer vertical height (a) away from the substrate by 20% (dashed line), while keeping the other parameters constant, resulted in a shift of the cusp position from $L=+/-0.5$ to +/-0.3. Alternatively, if the density of surface atoms ($\rho$) increases by a factor of 6 (dotted line), while the vertical layer height and strain parameters are kept at their initial values, results in an intensity increase between the Bragg points. As with the reflectivity observations, the simple model highlights ways that surface modifications can be observed when combined with sharp Bragg scattering.

Fractional rod scattering exhibits the same qualitative intensity variation as bulk rod scattering, but restricted to reconstructed surface layer interactions. The initial model for fractional rod intensity is the same as for the bulk, described above. Figure 3.5 shows the intensity for $(\frac{1}{2}, \frac{1}{2})(\frac{-1}{2}, \frac{-1}{2})$ symmetry equivalent rods with the initial model (solid line). Because the surface atoms are perturbed from their bulk positions, the resulting rod scattering results in a limited interaction between the top bulk layer and the surface layer. The periodicity and amplitude of rod oscillations provide information about which layers are interacting, as well as the strength of their interaction. The initial model results in a periodicity of $\Delta L = 1.0$, and corresponds with the bulk lattice spacing, defined as unity. The
second model involves shifting the vertical layer height \((a)\) away from the substrate 20\% (dashed line), while keeping the bulk scattering power and initial strain. For this model, the maximum amplitude shifts toward lower L-values, just as it did for bulk-rod scattering. Alternatively, increasing the atomic scattering strength \((\rho)\) by a factor of 6 (dotted line), while keeping the other parameters at their initial values, dampens the intensity oscillations. The combined model observations for fractional rods, therefore, provide direct evidence for height and density variations of surface reconstructions.

### 3.3 Fourier Analysis Techniques

Fourier Inversion techniques can circumvent the ”phase problem” of scattering to infer correct structural models based on experimental data. Fourier Inversion techniques take advantage of the relationship between structure factor from scattering amplitude \(|F|\) and real space electron density \((\rho)\) to determine the position of atoms in the unit cell. Inversion of experimental structure factors can then be used to determine relative electron density, using a Patterson Analysis, or absolute electron density, by Fourier Inversion Analysis. Finally, there are different algorithms that can be used to take advantage of computational power to quickly determine the correct structural model. Therefore, Fourier analysis provides a useful alternative to trial and error attempts to determine structural models.

#### 3.3.1 Electron Density

The scattering process is equivalent to a Fourier expansion of electron density in a crystal. Consequently, using the Fourier Series expansion to model electron distribution within a unit cell, combined with experimentally collected data, will aide structural modeling of sur-
faces. In general form, the Fourier expansion of electron density is given in eqn. 3.10. The electron density ($\rho$) is a function of real space coordinates (x,y,z). Whereas, the Fourier expansion is in Fourier space coordinates (n,p,q). Because the unit cell is a periodic boundary condition, the series coefficients ($C(n)$) are determined within the limits of the unit cell.

$$\rho(x, y, z) = \sum_{n,p,q=-\infty}^{+\infty} C(n, p, q)e^{-i2\pi\left(\frac{n}{a}x + \frac{p}{b}y + \frac{q}{c}z\right)} \quad (a) \quad (3.10)$$

$$C(n, p, q) = \int_0^a \int_0^b \int_0^c \rho(x, y, z)e^{-i2\pi\left(\frac{n}{a}x + \frac{p}{b}y + \frac{q}{c}z\right)}dV \quad (b)$$

The experimentally collected structure factors ($F_{hkl}$) for each diffraction peak are equivalent to the expansion coefficients $C(n,p,q)$ of the Fourier series. Thus the structure factors can be related to the real-space electron density, assuming that the phase factors can be known, as in eqn. 3.11(a). Taking advantage of the point symmetry of crystal structures, the electron density can be written as a function of the experimental structure factors, as shown in eqn. 3.11(c). The phase ($\phi_{hkl}$) is the complex component that is lost in the experimental observation. Therefore, each experimental diffraction intensity represents a Fourier Coefficient of the electron density expansion, and the more diffraction peaks observed the more accurate electron density can be determined.
\[ F_{hkl} = \int_0^a \int_0^b \int_0^c \rho(x,y,z)e^{-i[2\pi(h\frac{x}{a}+k\frac{y}{b}+l\frac{z}{c})]}dV \] (a)

\[ \rho(x,y,z) = \frac{1}{V} \sum_{h,k,l=-\infty}^\infty |F_{hkl}|e^{2\pi(i(h\frac{x}{a}+k\frac{y}{b}+l\frac{z}{c})-\phi_{hkl})} \] (b)

\[ \rho(x,y,z) = \frac{1}{V} \sum_{h,k,l=-\infty}^\infty |F_{hkl}|\cos[2\pi(h\frac{x}{a}+k\frac{y}{b}+l\frac{z}{c})-\phi_{hkl}] \] (c) (3.11)

### 3.3.2 The Patterson Function

The Patterson Function determines the relative electron density within a unit cell by using a density-density correlation function [44]. The density-density correlation function, defined in eqn.3.12(a), describes how atoms are distributed within a unit cell relative to other atoms in the unit cell. By taking advantage of the point symmetry of the crystal, the Patterson function can be re-written as a symmetric collection of diffraction intensities obtained experimentally, as shown in eqn.3.12(c).

\[ P(X,Y,Z) = \frac{V}{abc} \int_0^a \int_0^b \int_0^c \rho(x,y,z)\rho(x+X,y+Y,z+Z)dxdydz \] (a)

\[ P(X,Y,Z) = \frac{1}{V} \sum_{h,k,l=-\infty}^\infty |F_{hkl}|^2\cos[2\pi(h\frac{X}{a}+k\frac{Y}{b}+l\frac{Z}{c})] \] (b) (3.12)

An initial structural model can be obtained by determining the Patterson Function from experimental data. The symmetry of the surface is first inferred by determining which diffraction peaks have identical intensity. Symmetry equivalent intensities can then be av-
averaged to minimize instrumental errors in the data. Then, the Patterson map can be obtained from the averaged data to find relative atomic densities within the unit cell. An important consequence of the Patterson Function is its bias by strong diffraction peaks. The biased density map cannot effectively determine small structural changes, such as surface strains or density variations.

### 3.3.3 Simple Cubic Surface Patterson Map

The Patterson Map of the toy surface in Fig. 3.4 can be calculated to provide a useful example for understanding Patterson analysis. The general Patterson function in eqn. 3.12 can then be applied to the in-plane diffraction data calculated using the surface structure factor in eqn. 3.7. The resulting Patterson function is calculated in eqn. 3.13. The in-plane diffraction intensities used for the Patterson function were restricted to a set $H, K \epsilon [-2.0, 2.0]$, with intervals of 0.25. The in-plane lattice constants were defined to be 1Å. Thus, the Patterson gives the distribution of bond lengths throughout the unit cell as a function of in-plane lattice constant $(a)$.

\[
P_{\text{cubic}}(X, Y) = \sum_{h,k=-2.0}^{2.0} |F_{\text{cubic}}(H, K)|^2 \cos[2\pi(HX + KY)]
\]  
\[a = b = 1.0\]

The Patterson map of the toy surface, plotted in Fig. 3.6, highlights the advantages of using Patterson analysis. The map shows a contour plot of the Patterson function calculated using eqn. 3.13. Positive contours on the map indicate atomic correlations on the
Figure 3.6: The Patterson function shows the distribution of bond lengths based on in-plane diffraction in fig3.4. The real-space vectors ($\vec{a}_1, \vec{a}_2$) indicate the direction of the bond lengths. The peaks in the map indicate the percent of positive correlations with origin defined as 1. The scale is indicated by color ranging from blue (low percent correlation) to red (high percent correlation). The first two peaks away from origin represent an integer bond length, as indicated. The percent of correlation (intensity of peaks) drops toward the center of the unit cell, indicating that fewer atoms are correlated on the surface with those bond lengths. The smaller peaks between the integer positions arise from truncating the Fourier Expansion creating artificial harmonic "ghosts".

The Patterson analysis of the toy surface also illuminates the weakness of Patterson Mapping. Since the Patterson function is a Fourier expansion based by diffraction peaks, the distribution will be biased by which peaks are observed. Furthermore, the Patterson
function will also be biased by peaks which have the most intensity. Consequently, the Patterson map of the toy model from in-plane diffraction data only shows positive contours at multiples of bulk lattice bond lengths, even though the surface has a known strain. Also, Fourier expansions are susceptible to ‘ghost’ peaks which are higher frequency oscillations of the true Fourier peaks. For example, in Fig. 3.6 the Patterson map has smaller positive contours at half orders of lattice constants. The ghost peaks can provide misleading information about the surface structure. Despite the limitations, Patterson analysis provides valuable information for an initial structural determination.

### 3.3.4 Fourier Difference Map

The missing phase problem from diffraction experiments can be side stepped by assuming the model phase is close to the experimental phase [15, 24]. The electron density of the model structure is calculated using the relationship in eqn. 3.14(b). The phase of the model is obtained as the argument of the complex model structure factor calculation. If the model is then assumed to be close to the true structure, then the model phases can be assumed to be close to the true phases. Consequently, the experimental electron density can be calculated as a Fourier transform with the experimental structure factors and the model phase, as represented in eqn. 3.14(c). However, because the model is close to the experimental structure it is more useful to determine the difference between the model and the experiment. Thus, taking the difference in electron densities of the model and experiment, called the *Fourier Difference Map*, provides an effective tool for structural analysis. The calculation of Fourier Difference is presented in eqn. 3.14(a).
The Fourier Difference Map can determine either missing atoms or excess atoms in the structural model, but is strongly biased by the initial model. The initial assumptions of the model biases the map, because the phases used to determine the model bias which locations within the unit cell represent electron density. For example, if the model doesn’t initially have atomic sites that exist in the “true” structure, then the difference map will not show the unknown atomic sites because those sites don’t exist in the phases. Also, the limited Fourier expansion creates higher frequency ”ghost” peaks in the map, just as was shown in the Patterson analysis. The ghost peaks will exist as less intense positive or negative contours on the map. Therefore, the usefulness of the Fourier Difference can be limited based on the initial assumptions and data set available.
3.3.5 Simple Cubic Surface Difference Map

Figure 3.7: This figure shows a Fourier Difference map of the simple cubic structure. The map was calculated with the 'experimental data' from the model and diffraction data in Fig. 3.4 and the 'model data' calculated with a simple cubic terminated surface. Using eqn. 3.14, the resulting map shows positive contours for missing electron density in the model. The contour density shows surface atoms shifted away from the substrate lattice sites, indicated by dashed circles. The arrows indicate the direction of strain shift from substrate lattice sites toward the positive contours. The pseudo-symmetric unit cell is outlined by the dashed triangle. If there were deviations within the unit cell that did not follow the pseudo-symmetry averaging, they would not be observed in the resulting averaged map.
\[ \Delta \rho = \sum_{h,k} |F_{hk}^{\text{cube, rec}}| - |F_{hk}^{\text{cube, bulk}}| \cdot \cos[2\pi(xh + yk) - \alpha_{hk}^{\text{cube, bulk}}] \] (3.15)

The Fourier Difference Map on the simple cubic surface highlights the advantages of determining missing or excess electron density in the structure, as shown in Fig. 3.7. The structure factors for the "experimental" structure were calculated for the toy cubic model from eqn. 3.7. The "experimental" parameters used a bulk scattering density \((\rho = 1.0)\) with an in-plane strain \(\epsilon \sim 15\%\). The "model" structure factors were calculated for a simple cubic 4x4 unit cell, as seen in Fig. 3.4(b). The "model" phases were then obtained as the argument of the complex "model" structure factor. The Fourier difference map was then calculated using eqn. 3.14.

Figure 3.7 shows a contour map of the Fourier Difference function calculated using eqn. 3.14. The map shows only positive contours. By definition of the Fourier difference function, when there is missing density in the model the map will show positive contours. Whereas, when there is excess density in the model the map will show strong negative contours. The map clearly shows missing atomic density at the four surface atom positions matching the strained structure used in the calculation. The ideal bulk sites are indicated by dotted circles on the map. The observed positive contours are shifted away from the bulk sites by \(\sim 15\%\), toward the unit cell center. Thus, the Fourier Difference map provides absolute atomic positions of missing atoms within the unit cell, even when the atoms are slightly perturbed from the model.

The Fourier Difference map also highlights the possibility of surface strain and anisotropic static Debye-Waller factor that can result from interface interactions with adsorbed atoms. Adsorbed surface atoms are influenced by the interaction with the substrate which may
create strained surface structures when the substrate and surface atoms have different bond lengths. The strained structures are observed as a shift in atomic position from a substrate position. The surface atoms in the cubic structure have shifted away from the substrate positions, inward toward each other. However, not every unit cell will have the same surface position resulting in a distribution of different possible atomic positions. Since x-ray scattering averages across all unit cells, the distribution of atomic positions results in a distribution of electron density within the unit cell, as observed in the simple cubic Fourier Difference map. The continuous distribution is modeled as an anisotropic static Debye-Waller factor, which spreads the electron density in a single direction on the surface. Consequently, strain and surface distributions can be modeled accurately using Fourier Difference mapping of two-dimensional diffraction.
4.1 Si(111)7x7 Scattering Outline

In this section we will describe the model of Si(111)7x7 scattering, which is the basis for the Pb/Si(111)7x7 scattering. The structural model calculations are based on the DAS model presented in Fig. 2.8. First, the total Si(111)7x7 structure factor calculations will be provided, followed by modeling for specular reflectivity, in-plane diffraction, and rod scattering. Reflectivity provides initial Si 7x7 layer densities and heights, relative to the bulk. In-plane diffraction provides the in-plane Si atom positions for the 7x7 layers, and will show how pseudo-symmetry is utilized to simplify the model. Finally, rod diffraction will connect the in-plane and vertical atomic positions from diffraction and reflectivity.

The vertical and in-plane components of the structure factor will be split into three equations. First, the total Si(111)7x7 structure factor model will describe the vertical posi-
tions of the Si layers presented in Fig. 2.8. Then, the in-plane bulk Si(111) structure will be described for a 49 atom 7x7 unit cell. Finally, the in-plane structure of the three 7x7 reconstructed layers will be described using pseudo-symmetry.

4.1.1 Total Si(111)7x7 Structure Factor

The total structure factor for the Si(111)7x7 system is calculated by combining the bulk Si(111) and the Si_7x7 structure factors. The model follows the DAS model presented in Fig. 2.8 [14, 15, 16, 17, 18]. However, the origin of the system, both in-plane and vertically, is defined as layer_3a. Consequently, the total structure factor is:

\[
F_{total_{Si}} = F_{bulk_{Si}(111)} e^{i2\pi \frac{(H+K)}{3}} + F_{2b}(z_{2b}, \Delta_{2b}) + F_{2a}(z_{2a}, \Delta_{2a}) \\
+ F_{Si-7x7}(z_{1b}, z_{1a}, z_{Ad}, \Delta_{1b}, \Delta_{1a}, \Delta_{ad}, \xi_{1b}, \xi_{ad}) e^{iQ \cdot \vec{c} \cdot \frac{1}{2}} \\
\]

(4.1)

\[
F_{bulk_{Si}(111)} = \text{equation 4.2} \\
F_{2b} = F_{3b} e^{iQ_1 (\frac{1}{2} + z_{2b})} e^{-\frac{1}{2} Q_2^2 \Delta_{2b}^2} \\
F_{2a} = F_{3a} e^{iQ_1 (\frac{1}{2} + z_{2a})} e^{-\frac{1}{2} Q_2^2 \Delta_{2a}^2} \\
F_{Si-7x7} = F_{layer-1b}(H, K, \xi_{1b}) e^{iQ_1 (\frac{1}{2} + z_{1b})} e^{-\frac{1}{2} Q_2^2 \Delta_{1b}^2} \text{ Equation 4.9(a)} \\
+ F_{layer-1a}(H, K) e^{iQ_1 (\frac{1}{2} + z_{1a})} e^{-\frac{1}{2} Q_2^2 \Delta_{1a}^2} \text{ Equation 4.9(b)} \\
+ F_{Adatoms}(H, K, \xi_{ad}) e^{iQ_1 (\frac{1}{2} + z_{ad})} e^{-\frac{1}{2} Q_2^2 \Delta_{ad}^2} \text{ Equation 4.9(b)}
\]

where the in-plane structure of the bulk unit cell (and layers 3a/3b) is calculated for a
7x7 unit cell area in eqn. 4.2. To simplify the discussion here, the in-plane structure for the three Si 7x7 layers will be calculated later in eqn. 4.9. Also, vertical momentum transfer is given as \( Q_z = \frac{2 \pi L}{c} \) is given in units of Å\(^{-1}\).

![Diagram of Si(111)7x7 layers](image)

**Figure 4.1:** This figure shows the height parameters for the Si(111)7x7 model. The parameters displace the Si layers from the bulk Si(111) lattice spacing.

The vertical origin for the model is layer-3a, as shown in Fig. 4.1. However, the in-plane origin is given as layer-1b, as seen in Fig. 2.8. This section will focus on the vertical shift, and the next section will describe the in-plane shift. A single bulk double layer stacking has a vertical shift of \( \left( \frac{c}{12} \right) \), while the distance between to double layers (3a-2b) is \( \left( \frac{c}{4} \right) \). Each surface layer has several parameters which shift the layers relative to their ideal positions. The Si 7x7 layers are assumed to remain close to ideal bulk Si(111) heights. Consequently, the height for each layer (2b,2a,1b,1a) is calculated as the ideal (111) height with a displace-
ment parameter \((z_j)\), which represents a small deviation. Secondly, A vertical DW factor \((\Delta^2_j)\) accounts for two different types of average atom displacements: thermal vibrations, and variations for different unit cells. Atomic thermal vibration, relative to ideal positions, results in a Gaussian distribution of electron density \(e^{-\frac{1}{2}Q^2\Delta^2_j}\). Also, unit cells can have defects which result in displacements of atoms from their ideal location. For example, one unit cell can have a 1a-Ad layer distance of 1.5Å, whereas another unit cell can have a 1.6Å distance. X-ray scattering *averages* these position deviations, resulting in another contribution to the Gaussian distribution parameter \((\Delta^2_j)\). Finally, in-plane displacement parameters \((\zeta_j)\) shift atoms in the Si 7x7 layers, and will be described later.
4.1.2 In-plane Bulk Structure

Here we will describe the bulk Si(111) structure factor used for reflectivity and rod scattering. The bulk Si (111) unit cell has six layers per unit cell:

\[
F_{\text{bulk Si}(111)} = F_{\text{double-layer}} \frac{1 + e^{i2\pi \frac{H+K}{\sqrt{3}}} + e^{-iQz\sqrt{3}} + e^{i2\pi \frac{2H+K}{\sqrt{3}}} e^{-iQz\sqrt{3}}}{1 - e^{-iQz\sqrt{3}}} \tag{4.2}
\]

\[
F_{\text{double-layer}} = (F_{3a} + F_{3b} e^{-iQz\sqrt{3}})
\]

49 atom 7x7 unit cell structure factor

\[
F_{3a} = 1 + e^{i2\pi(H)} + e^{i2\pi(2H)} + e^{i2\pi(3H)} + e^{i2\pi(4H)} + e^{i2\pi(5H)} + e^{i2\pi(6H)} \quad \text{(Edge Atoms)}
\]

\[
+ e^{i2\pi(K)} + e^{i2\pi(2K)} + e^{i2\pi(3K)} + e^{i2\pi(4K)} + e^{i2\pi(5K)} + e^{i2\pi(6K)} \quad \text{(Edge Atoms)}
\]

\[
+ e^{i2\pi(H+K)} (1 + e^{i2\pi(H)} + e^{i2\pi(2H)} + e^{i2\pi(3H)} + e^{i2\pi(4H)} + e^{i2\pi(5H)})
\]

\[
* (1 + e^{i2\pi(K)} + e^{i2\pi(2K)} + e^{i2\pi(3K)} + e^{i2\pi(4K)} + e^{i2\pi(5K)}) \quad \text{(Center Atoms)}
\]

\[
F_{3b} = e^{i2\pi \frac{2H+K}{\sqrt{3}}} (1 + e^{i2\pi(H)} + e^{i2\pi(2H)} + e^{i2\pi(3H)} + e^{i2\pi(4H)} + e^{i2\pi(5H)} + e^{i2\pi(6H)})
\]

\[
* (1 + e^{i2\pi(K)} + e^{i2\pi(2K)} + e^{i2\pi(3K)} + e^{i2\pi(4K)} + e^{i2\pi(5K)} + e^{i2\pi(6K)}) \quad \text{(Center Atoms)}
\]
4.2 Clean Si(111)7x7 Reflectivity

Figure 4.2: This figure shows specular reflectivity from the clean Si(111)7x7 interface.\(^{(a)}\)
The real-space structure of bulk Si(111) is based on two inter-penetrating FCC lattices, shown as red (dashed outline circles) and blue (solid outlined circles). The inter-penetrating lattices are separated by a fixed distance \((\frac{c}{12})\). Each lattice has the same double layer stacking \((a,b)\). Each set double layers is separated by \((\frac{c}{3})\).\(^{(a)}\) The structure factor calculation for for each layer and phase difference for the inter-penetrating lattice modify the standard bulk term. The layer stacking provides different termination possibilities for the Si(111)surface.\(^{(c)}\)

The reflectivity for an experimental clean Si(111)7x7 crystal was fit with three possible surface termination models. The first model (dashed line) is a layer-1a terminated model given in eqn. 4.3. The second model is a layer-1b terminated model (dotted line), which violated, also described in eqn. 4.3. The best fit (solid line) to the data is the Si(111)7x7 model presented in eqn. 4.5.
The clean Si(111)7x7 surface provides an example of using surface reflectivity to understand a model of complicated surface reconstructions. Bulk Si(111) follows the diamond structure of two inter-penetrating FCC lattices, as shown in Fig. 4.2(a). The first lattice, shown as red atoms with dashed outlines, contributes three atoms per unit cell. The second lattice is given by blue atoms with solid outline, and contributes a further three atoms per unit cell. Each atom in the unit cell is given by the term in the numerator of the structure factor, as shown in Fig. 4.2(b). The double layer stacking is given by an extra term, next to the fraction, which further restricts which Bragg points exhibit observed intensity. The new terms are then divided by the standard bulk geometric term, from eqn. 3.5, to give the complete structure factor for a Si(111) crystal. The new diamond structure terms limit the number of observed Bragg peaks, so that only odd multiples of integer L-values (3, 9,...) will result in Bragg scattering.

The experimental observations on the clean Si(111)7x7 surface show that it doesn’t follow a simply terminated bulk structure, as shown in Fig. 4.2(c). The figure shows intensity from a clean Si(111)7x7 surface held at 30°C, and exhibits the expected strong intensity with multiples of three in reciprocal lattice units (r.l.u.). However, the data shows complicated oscillatory behavior between the Bragg peaks. As the previous cubic toy model example showed, the oscillatory behavior can be fit by adding extra surface layers with modified lattice spacing and density.

The complicated unit cell provides several possible surface terminations, which have previously shown to not fit the observed Si(111)7x7 surface [18]. The bulk Si(111) structure factor equation, given in Fig. 4.2(b), terminates the surface with layer-1a. However, an alternate surface termination could be a single layer-1b stacking above the bulk, which
would violate the double stacking scheme, which is given:

\[ F_{S_i(111)7x7} = F_{\text{surface}} + F_{S_i} \quad (4.3) \]

\[ F_{S_i} = \text{Given in Figure 4.2(b)} \]

\[ F_{\text{surface}} = \rho_{\text{single}} e^{i2\pi(z)} \quad \text{Layer-1b Stacking Termination} \]

\[ (4.4) \]

The intensity from the bulk terminated model does not compare well with the observed data. The model over-reports intensity between the L=3,9 bragg peaks. Also, the layer-1b stacking model does not fit the observed data. The intensity from this model under-reports the intensity between the L=3,9 Bragg peaks. The resulting model fits then suggest that a model with some combination of double layer stacking fits the Si(111)7x7 surface.

The previously proposed Si(111)7x7 model \([14, 18]\) gives the best fit to the data. The model calculations use eqn. 4.1 with \(H=K=0\), and the Si-7x7 structure factor defined as:

\[ F_{S_i-7x7} = \rho_{1b} e^{i\vec{Q}(z_{1b})} e^{-\frac{i}{2}Q_z^2\Delta z_{1b}} \quad \text{Layer-1b} \]

\[ + \rho_{1a} e^{i\vec{Q}(z_{1a})} e^{-\frac{i}{2}Q_z^2\Delta z_{1a}} \quad \text{Layer-1a} \]

\[ + \rho_{ad} e^{i\vec{Q}(z_{ad}+z_{ad})} e^{-\frac{i}{2}Q_z^2\Delta z_{ad}} \quad \text{Adlayer} \]

\[ (4.5) \]

where the density parameters \((\rho_{1b}, \rho_{1a}, \rho_{ad})\) represent average atomic density, and take the place of in-plane atomic positions. The in-plane atomic positions will be described in the next section. As can be seen, the height parameters in the equation above are relative to layer-1b. The explicit origin shift \((e^{iQ_z \cdot c_{12}})\) in eqn. 4.1 properly shifts \(F_{S_i-7x7}\), above, to
the origin at layer-3a.

This model has the first layer, above the bulk, with a density $\rho_{1b} = \frac{47}{49}$, followed by a second layer, above the bulk, with $\rho_{1a} = \frac{42}{49}$, and a third layer, above the bulk, with $\rho_{ad} = \frac{12}{49}$.

The heights of layers(1b,1a) are assumed to be ideal bulk double layer heights. Thus the height parameters give deviations from ideal positions ($\delta_{1b} = 0.02 \pm 0.03\,\text{Å}$, $\delta_{1a} = 0.08 \pm 0.03\,\text{Å}$). The third layer height is given relative to layer-1a ($\delta_{ad} = 1.80 \pm 0.2\,\text{Å}$). The intensity from this fit correctly reproduces all of the features in the experimental data. Therefore, this model will provide the initial constraints to help determine the three dimensional atomic structure and provides an example for how to solve the Pb/Si(111)7x7 structure.

### 4.3 Clean Si(111)7x7 Surface Diffraction

In-plane structural modeling of the Si(111)7x7 surface requires understanding the Hexagonal structure. First, in-plane hexagonal symmetry of the 7x7 will be introduced. Then, the pseudo-symmetry of the 7x7 unit cell will be presented. The pseudo-symmetry provides an extra symmetry restriction on top of the six fold symmetry, which simplifies the model. The pseudo-symmetric 7x7 structure factor calculation will then be presented. Finally, the model 7x7 unit cell fit to experimental Si 7x7 in-plane diffraction will be described.

#### In-plane Hexagonal Symmetry

The stacking in the Si(111) crystal follows hexagonal close packing symmetry. In this symmetry the in-plane real-space ($\vec{a}_1^*, \vec{a}_2^*$) and reciprocal-space vectors take on multiples of $60^\circ$. Typically, the in-plane real-space lattice vectors are $120^\circ$ apart, as shown for the Si(111)7x7 unit cell in Fig. 2.8. Consequently, the reciprocal-space unit vectors are $60^\circ$
apart, by application eqn. 3.2. The relationship between real-space lattice constants and reciprocal-space integers in hexagonal coordinates, is conveniently provided by B.E. Warren [26] in his chapter on crystal axis pp.15-26 and is reproduced here:

\[ \vec{Q} = \frac{2\pi}{d_{hkl}} = \sqrt{\frac{4}{3}(H^2 + HK + K^2) + \frac{L^2}{c^2}} \]  \hspace{1cm} (4.6)

\[ a_H = 3.84\text{Å} \quad c_H = 9.4\text{Å} \]  \hspace{1cm} (4.7)

The hexagonal unit cell lattice constants (a,c) relate the observed diffraction data to the unit cell dimensions of the bulk crystal. The lengths of in-plane and perpendicular real-space vectors are defined relative to the known lattice constants of the bulk crystal. Knowing the in-plane lattice constants means any observed diffraction peak is referenced relative to the known real-space distance of the bulk crystal. Thus any real-space plane distance can be determined for any observed fractional or bulk diffraction peak observed. For the Pb/Si(111)7x7 studies the diffraction data are referenced to the bulk Si(111) lattice constants, given in eqn. 4.7.

**Pseudo-symmetry Operations of the 7x7 unit-cell**

The large Si(111)7x7 unit cell can be further sub-divided into a pseudo-symmetric unit cell, which is indicated by the outlined triangle in Fig. 2.8. The sub-unit cell significantly reduces the number of atoms required to model, because the symmetry equivalent atoms through out the 7x7 unit cell follow the operations of atoms within the pseudo unit cell. Moreover, any metal wetting layer model can be simplified by utilizing the pseudo-symmetry operations. The pseudo-symmetry operations described in eqn. 4.8 are split into
three levels for each symmetry operation type:

\[ F_{Total\times7} = F_{Half-cell}(H, K) + F_{Half-cell}(K, H) \]  
\[ = \text{Faulted + Unfaulted unit cell halves} \]  
\[ F_{Half-cell}(H', K') = F_{pseudo-cell}(H', K') + F_{pseudo-cell}(H' + K', -K') \]  
\[ + [F_{pseudo-cell}(-H', K' + H') + F_{pseudo-cell}(K', -H' - K')]e^{2\pi i \Gamma H} \]  
\[ + [F_{pseudo-cell}(-K' - H', H') + F_{pseudo-cell}(-K', -H')]e^{2\pi i \Gamma (H+K)} \]  
\[ \Gamma = \text{Any integer which corresponds to the lattice.} \]  
\[ \text{(i.e. } \Gamma=7 \text{ for 7x7 lattice, or } \Gamma=8 \text{ for an 8x8 lattice).} \]  
\[ F_{pseudo-cell}(H'', K'') = \text{This is the sub-unit cell structure factor of any general model} \]

The first level of symmetry operation involves the mirror symmetry separating the faulted and unfaulted halves of the unit cell. The unfaulted half unit cell is then given by the function \( F_{Half-cell}(H, K) \). The faulted half is calculated as the mirror of the faulted half along with a phase shift toward the opposite end of the unit cell, represented by the second term in eqn. 4.8. The \( \Gamma \) parameter is an integer which describes the amount of phase shift required to shift the origin. The clean Si(111)7x7 unit cell has a \( \Gamma=7 \), whereas an 8x8 lattice would have a \( \Gamma=8 \).

The second level of symmetry operations occurs within the unit cell half. The unit cell half can be broken into six sub-unit triangles, with the triangle outlined in Fig. 2.8.

\footnote{Note: The actual mirror symmetry operation applied in this thesis was not the general form given. Computationally the shift was written as: \( F_{Half-cell}(-H, -K)e^{2\pi i \Gamma (H+K)} \). This operation only works because of pseudo-symmetry restriction. Without the pseudo-symmetry restriction, the operation described in eqn. 4.8 must be used.}
representing the sub-unit cell. The operations force all atoms within the unit cell half to be equivalent across the dashed boundary lines of the sub-unit cell. However, an extra consideration must be made for atoms which lie along the symmetry lines. Atoms along the symmetry lines will be counted twice during the operations. Therefore, a scale factor of 0.5 must be applied to all atoms along the symmetry lines in the model.

The final level of symmetry operation is the pseudo-symmetric sub-unit cell. This function accounts for all model atoms on the surface, as well as any strain or occupancy modifications. However, extra consideration must be made for any atom along the pseudo-symmetry lines of the cell; because atoms along the cell will be double counted, adding a strain parameter which shifts the atoms away from the symmetry line will artificially reduce the occupancy of the atom. Furthermore, shifting the atom away from the symmetry line will create two equivalent atoms on either side of the symmetry line. Therefore, special restrictions must be placed on atoms along the symmetry lines.

**Structure Factor for the In-plane Si(111)7x7 Unit cell**

Utilizing the pseudo-symmetry operations outlined in section 4.3, the structure factor for the total Si(111)7x7 unit cell is reduced to the limited pseudo-symmetric unit cell of 13 Si-atoms. The atoms within the sub-unit cell, taken from Fig. 2.8, are added to the structure factor, for each layer, in eqn. 4.9. Importantly, the atoms along the pseudo-symmetry lines have a factor of $\frac{1}{2}$ applied to them, because of the double counting described in the pseudo-symmetry section 4.3.
\[ F_{\text{Si-7x7}} = F_{\text{layer-1b}} + F_{\text{layer-1a}} + F_{\text{Adatoms}} \] (4.9)

\[ F_{\text{layer-1b}} = \frac{1}{2} [e^{i2\pi(1+\zeta_{1b})H} + e^{i2\pi(2-\zeta_{1b})H} + e^{i2\pi(3+\zeta_{1b})H}] \]
\[ + \frac{1}{2} [e^{i2\pi(2H+K)} + e^{i2\pi(4H+K)} + e^{i2\pi(4H+2K)}] + e^{i2\pi(3H+K)} \] (a)

\[ F_{\text{layer-1a}} = e^{i2\pi\frac{1}{3}(2H+K)} \left[ \frac{1}{2} + e^{i2\pi H} + e^{i2\pi 2H} \right] \]
\[ + \frac{1}{2} e^{i2\pi\frac{1}{3}(2H+K)} \left[ e^{i2\pi(2H+K)} + e^{i2\pi(3H+K)} \right] \] (b)

\[ F_{\text{Adatoms}} = \frac{1}{2} [e^{i2\pi(2H+K)(1+\zeta_{ad})} + e^{i2\pi(4H+K+\zeta_{ad}(H+2K))}] \] (c)

The Si(111)7x7 in-plane structure factor has two strain parameters which can be varied to fit experimental diffraction data. Both strain parameters in the model are fractions of an in-plane lattice spacing (a\textsubscript{H}). Consequently, the strain parameters must be multiplied by the lattice spacing to obtain an absolute real-space value. First, the Si-atoms along the edges of the unit cell in layer-1b have a dimerization parameter (\(\zeta_{1b}\)). Previous X-ray diffraction studies showed that the Si-atoms along the edges of the unit cell obtain a dimerization of 0.6±0.15Å per atom [15]. The adatom layer also has an in-plane strain (\(\zeta_{ad}\)) which pulls the adatoms toward the center of the unit cell half [15]. However, no previous study has proposed an value of the strain, and it is likely temperature dependent.
In-plane Diffraction Map of Clean Si(111)7x7

Figure 4.3: This figure shows experimental data and model fit for a clean Si(111)7x7 in-plane diffraction map. The surface was obtained on a clean Si(111)7x7 surface at \(\sim 30^\circ C\). The model was calculated based on the Si(111)7x7 model presented in Fig. 2.8, and using the structure factor from eqn. 4.9. Each position on the map represents a diffraction peak with integrated intensity proportional to the area of the half circle. The experimental data is represented by the left semi-circle. The model fit is represented by the right semi-circle. Bulk Si(111) integer diffraction spots are labeled and indicated by hexagons. The mirror symmetry lines for six-fold symmetry are indicated as solid lines. The mirror symmetry line within the 7x7 unit cell is indicated as a solid line along the h=k direction. Pseudo-symmetry lines within the 7x7 unit cell are indicated as dashed lines, and symmetry operations about the pseudo-symmetry lines indicated by ovals. The model fit to the data gave atomic positions for the Si dimerization \(\sim 0.4\pm0.2\text{Å}\), as well as Si adatom radial shifts \(\sim 0.0\pm0.2\text{Å}\).
Clean Si(111)7x7 in-plane diffraction will provide insight for how to fit experimental diffraction data using a known structural model. Figure 4.3 shows a diffraction pattern for the clean Si(111)7x7 surface taken at ∼30°C. The map shows 7 fractional spots between each bulk Si(111) position, which supports the 7x7 unit cell area of the model. Also, the diffraction peaks are symmetric about the h=k symmetry line, meaning the (0, 0) equals the (0, 7). Therefore, the diffraction map shows that the Si(111)7x7 surface follows six-fold symmetry, unlike the bulk Si(111) substrate which follows three-fold symmetry.

The model was previously solved using real-space [14] as well as scattering techniques [15, 16]. Consequently, fitting the data in fig. 4.3 requires only shifting the in-plane strain parameters (ζ_{1b}, ζ_{ad}) of the structure factor in eqn. 4.9. Using χ² analysis with the data in fig. 4.3, the model fit gave dimer strain ζ_{1b} = ∼0.4±0.2Å and adatom strain ζ_{ad} = ∼0.0±0.2Å.

It is useful to discuss the relationship between diffraction peaks and the in-plane strain parameters of the 7x7 model, because they provide insight for modeling the Pb/Si(111)7x7 surface. First, because the atomic shifts of the dimer-atoms occur along the edges of the unit cell, the dimer parameter will strongly affect peaks without mixed real-space coordinates: (h,0),(0,k), and their symmetry equivalents. Second, the Si adatom in-plane atomic motion occurs toward the center of the faulted/unfaulted unit cell half [17]. Thus, any adatom shift will affect multiple diffraction intensities. This relationship suggests a useful insight: if peaks along high symmetry directions are more intense than peaks not along symmetry directions, then the model should have atomic motions along the edges of the unit cell. Alternatively, if peaks away from high symmetry directions have more intensity, then atomic motion occurs within the unit cell.
4.4 Si(111)7x7 Bulk/Fractional Rods

Understanding the clean Si(111)7x7 rod scattering is important because they are the basis for determining the Pb/Si(111)7x7 rods. The surface structure has already been determined by reflectivity and in-plane diffraction, but rod scattering will provide extra sensitivity Si-atom vertical positions. Also, the reconstructed surface follows six-fold symmetry, while bulk Si(111) exhibits three-fold symmetry. Furthermore, rod scattering will determine any deviation of the surface structure from six-fold symmetry of the model, which in-plane scattering cannot distinguish.
Si(111)7x7 Bulk Rod Symmetry

Figure 4.4: This figure shows bulk Si(111) crystal truncation rods, reproduced from Ph.D. dissertation of Chinkyo Kim [43]. The Si(111) crystal exhibits three fold symmetry resulting in three different types of surface truncation rods. The first rod type has Bragg points at \( L=0,3 \) and is colored black. The second type has Bragg points at \( L=1,4 \) and is colored green. The final rod type has a single Bragg point at \( L=5 \) and is colored red. The hexagonal lattice shows bulk-Si(111) in-plane scattering positions \((H,K,L)\), with the \( L\)-value indicating the location of Bragg scattering. The hexagonal lattice shows the clear three-fold symmetry of the Si(111) crystal structure.

Rod scattering from the bulk structure factor follows three-fold symmetry, resulting in three unique types of rod profiles, as shown in Fig. 4.4. The figure shows six-quadrants with the symmetry equivalent rods color coded. The black profile rods have Bragg points at \( L=0,3 \).
The Green profile rods have Bragg points at \( L = 1,4 \). The red profile rods have a single Bragg point at \( L = 5 \). The ideally terminated rod profiles provide a basis for determining how the complex reconstructed surface modifies the intensity. The surface follows a six-fold symmetry, and will then have rods in all six quadrants be symmetry equivalent to each other, unlike the bulk rods. Therefore, the Si(111)7x7 surface will exhibit different fractional and bulk rod scattering behavior.

**Si(111)7x7 Fractional Rod Scattering**

The Si(111)7x7 fractional rod structure factors are calculated by including vertical height parameters for each layer, as represented in eqn. 4.10. The sub-unit cell structure factors are the same as calculated in eqn. 4.9, with the strain parameters included. Fractional rod data are insensitive to the bulk layers below the surface. Consequently, Si layer-1b is defined at \( z = 0 \) on the surface in the fractional rod analysis. The vertical height parameters \((z_1, z_2, z_3)\) of the model represent deviations from the ideal positions in fig. 2.7. Also, the parameters are the same as the heights determined from reflectivity modeling. Thus, fractional rod data provide a connection between in-plane diffraction and reflectivity data.

\[
F_{Si-7x7} = F_{layer-1b}(H, K, \zeta_{1b})e^{iQ_zz_{1b}}e^{-\frac{1}{2}Q^2\Delta^2_{1b}} \\
+ F_{layer-1a}(H, K)e^{iQ_z(c\frac{1}{2}z_{1a})}e^{-\frac{1}{2}Q^2\Delta^2_{1a}} \\
+ F_{Adatoms}(H, K, \zeta_{ad})e^{iQ_z(c\frac{1}{2}z_{1a} + \zeta_{ad})}e^{-\frac{1}{2}Q^2\Delta^2_{ad}}
\]  
(4.10)
Figure 4.5: This figure shows model fits to experimental structure factor of the clean Si(111)7x7 rod data, as a function of perpendicular reciprocal lattice units (L). Each rod scan was taken on the same clean surface at 30°C. The ($\frac{3}{7}$, 1) and ($\frac{6}{7}$, 1) were re-scaled to fit on the figure. The model fits used the structure factor model given in eqn. 4.10. The in-plane strain parameters were found to be $\zeta_{1b} = 0.6 \pm 0.1$ Å and $\zeta_{ad} = 0.2 \pm 0.1$ Å. Also, the vertical height parameters were found to be $z1 = -0.01 \pm 0.01$ Å, $z2 = -0.05 \pm 0.02$ Å, and $z3 = 2.3 \pm 0.1$ Å.

Clean Si(111)7x7 scattering rods show that the model of the clean surface can accurately reproduce the data, as shown in Fig. 4.5. Periodicity and amplitude of oscillations in fractional rod data indicate the length and strength of interactions between layers. For example, the ($\frac{3}{7}$, 1) rod shows the strongest oscillatory behavior. The periodicity of the oscillations occurs with a $\Delta L \sim 3.0$ r.l.u., which is translated into a real-space distance $d \sim \frac{c}{\Delta L} = 3.13$ Å. The distance immediately rules out the interaction between layers 1a-1b, because their inter-layer distance is $\sim 0.78$ Å. Thus, the interaction must occur between either 1b-adlayer or 1a-adlayer. The amplitude of oscillation in the ($\frac{3}{7}$, 1) rod also indicates
that the interaction between the layers is strong, because a weaker interaction would produce a much weaker amplitude like the \( \left( \frac{6}{7}, 0 \right) \) rod. Therefore, understanding the features of rod scattering provide key insights to initial model analysis on the surface.

The previously proposed clean Si(111)7x7 model accurately reproduces the fractional rod data. The model structure factor calculation is given by eqn. 4.10. Subsequently, the fractional rod data were fit with the in-plane strain \( (\zeta_{1b}, \zeta_{ad}) \) and layer height \( (z_1, z_2, z_3) \) parameters. The position of the cusp in the \( \left( \frac{3}{7}, 1 \right) \) model fit gives the adatom layer height \( z_3 \sim 2.3 \pm 0.1 \text{Å} \) above the Si-1a layer. The model height combined with the oscillation periodicity of \( \sim 3.1 \) indicates that the rod corresponds to the interaction between 1b-adatom layers. Furthermore, the depth of the oscillation below \( L = 3.0 \) relative to the cusp at \( L = 4.5 \) depends on the interaction between the in-plane strain parameters of the model. The fit indicates that the dimer parameter \( \zeta_{1b} = 0.6 \pm 0.1 \text{Å} \) and \( \zeta_{ad} = 0.2 \pm 0.1 \text{Å} \). The final model parameters, determined from the \( \left( \frac{3}{7}, 1 \right) \) rod, reproduced the observed data for the \( \left( \frac{6}{7}, 0 \right) \) and \( \left( \frac{6}{7}, \frac{1}{7} \right) \) rods as well.

Fitting rod data provides the linchpin necessary to determine the correct model of the surface, which reflectivity and in-plane diffraction cannot separately provide. Reflectivity provides vertical height and average layer density, but cannot distinguish in-plane atomic positions. Independently, in-plane diffraction provides in-plane atomic order, but cannot distinguish vertical atomic heights. Moreover, in-plane diffraction data can be fit with degenerate models, because of missing phase information in the data. Rod data provide the connection between vertical heights from reflectivity and in-plane atomic positions from diffraction data. Therefore, combining all three scattering geometries in data analysis minimizes the model degeneracy.
Chapter 5

Details of Data Collection and Analysis

5.1 Sample Holder

The sample stage has several layers with different technical advantages, such as increased thermal stability and temperature sensitivity. Figure 5.1 shows the different technical aspects on the sample stage. The copper block is the base of the sample holder and operates as the cold sink for the Si(111) samples. The sample temperature is regulated using direct filament heating to the back side of the samples. The Si(111) samples rest on the Molybdenum plate (Mo-block) and are thermally and electrically isolated from the Copper block using the three Sapphire standoffs. Sample temperature is inferred using thermal sensors connected to the bottom of the Mo-block and are also used for temperature regulation. Finally, the sample is held on the Mo-block using a locking mechanism (not pictured) which is engaged using the ball bearings on either side of the Mo-block.
Figure 5.1: This figure shows the Top and Side view perspectives of the sample stage assembly in the UHV chamber. The sample rests on top the Mo-block assembly, which has thermal sink connections using Sapphire standoffs. The standoffs are connected to the Cu-block which acts as the thermal sink. The heat input is supplied by the filament, which irradiates the back of the Si-samples. The sample temperature is determined indirectly by T.C. connections to the bottom of the Mo-block.
5.2 Low Energy Diffraction (LEED)

Figure 5.2: The LEED assembly rests above the sample location on the Missouri Chamber. The LEED assembly is free to rotate into and out-of position under UHV. The cooling stage used to increase pumping efficiency in order to achieve a good Si(111)7x7 surface, is also indicated in the figure.

Low Energy Electron Diffraction (LEED) provides a simple and easy way to determine macroscopic order on the surface. LEED elastically scatters a beam of electrons from a sample and views the diffraction on a photo-fluorescent screen. Electrons interact strongly with atoms in the sample, which limits the penetration depth. LEED is then limited to probing the top few layers of the surface. Also, the strong interaction leads to multiple scattering
events which can change diffraction intensity as a function of beam energy as well as cause extra diffraction peaks to be observed. The strong interaction makes LEED a quick and easy way to determine surface preparation and initial analysis of surface processes.

The physical position of the LEED system is indicated in Fig. 5.2. The LEED gun, itself, is approximately 1 ft in length. The gun extends into the chamber and is positioned with the front screen approximately 70cm from the sample surface. The gun operates at a pressure of $10^{-6}$ Torr or less. The phosphorescent screen glows green when bombarded by electrons, and is approximately 15cm in diameter. Understanding the physical location and dimensions of the LEED allow for direct indexing of diffraction pattern peaks observed on the screen.
The creation of a LEED image is dependent on the electronic operation of the gun, from the energy of outgoing electrons to intensity of diffraction spots observed on the screen. Figure 5.3 shows all of the individual control parameters that determine the operation of the LEED. The energy of outgoing electrons is controlled by the primary beam energy, which creates a negative potential between the filament and the sample from 0-500eV. The num-
ber of electrons that are transmitted by the filament is controlled by the Emission voltage, which creates a positive potential that attracts electrons. The Focus control creates an electrostatic 'lens' to focus the on the screen, after they scatter from the sample. Low energy imaging, with primary beam energy below 100 eV, has significant background scattering from electrons that don’t maintain the primary beam energy. The Retarding potential limits the background scattering from electrons that don’t have primary beam energy by attracting them to the gun instead of the screen. The Screen potential increases the observed intensity on the phosphorescent screen by creating a positive potential that attracts more electrons. The increased potential also increases the background intensity observed on the screen. Finally, the contrast reduces the amount of spurious background electrons scattering from the surface to the LEED screen. All of these control parameters make good LEED imaging difficult for dynamic processes on the surface.
LEED images of Si(111)7x7 interface

Figure 5.4: This figure shows a LEED image taken on the Si(111)7x7 at ∼30°C. The center of the image is obscured by the profile of the LEED electron gun. The dark spots indicate diffraction peaks. The (0,0), (1,0), and (0,1) spots are indicated for reference. A collection of smaller spots in a hexagonal pattern are seen connecting the bulk peaks.

The LEED analysis of the Si(111)7x7 surface provides a qualitative determination of effective preparation parameters, such as temperature and annealing time. The surface was prepared in the chamber shown in Fig. 5.3. After the Si(111)7x7 surface was prepared and cooled to ∼30°C, the LEED was positioned above the sample. The image shown in Fig. 5.4 was obtained with the following gun parameters: Primary=38 V, Retarding = 215
V, Focus= 32V, Contrast=4V, Screen=500V, Filament Current=1.7A, and Emission=0.2A. Small deviation from any of the parameters resulted in a much less distinguished image. The sample was rotated off center so that the origin diffraction spot could be indexed, as indicated in the figure. The diffraction pattern produces a hexagonal symmetry which has previously been observed using LEED analysis [21, 22], and similar to X-ray diffraction patterns [15]. The most distinguished bulk spots have been indexed in the image. The diffraction spots nearest to the bulk positions are strongest, which is similar to X-ray diffraction on the Si(111)7x7.

5.3 Data Collection/Analysis

5.3.1 Geometry of Scans

This section outlines corrections to the data which are related to the geometry of the scans. First, the geometrical effects which give rise to the corrections will be discussed. The geometry depends on the mode of scanning used to collect the data, such as fixed incoming angle ($\alpha$-fixed) or fixed outgoing beam ($\beta$-fixed). Then, the calculations for the geometrical corrections will be discussed. Finally, a comparison between two different scans of the Pb/Si(111) $\alpha$-phase will be presented. The comparison will show that geometry corrected data will result in data independent of geometry used.
Active Area Corrections

![Active Area Corrections Diagram](image)

Figure 5.5: This figure shows the geometry of active area corrections on the surface. The angle between the slits ($\delta = \phi_i + \phi_f$) is related to the geometry angles outlined in Fig. 3.1.

(a) When the constrained incoming beam doesn’t spill off the sample and the scattered beam is constrained by detector slits, the active area is the parallelogram formed by the two slit functions. (b) The reduced active area occurs when the area of the incoming beam, projected onto the sample, is smaller than the parallelogram calculated in (a). The reduced active area region occurs for rod scattering, when the perpendicular component of the incoming beam causes the reduced region.

The slit projections of the incoming beam and detector, onto the sample surface, changes the amount of incoming beam bathing the sample, as well as scattered beam collected by the detector. The incoming beam is constrained parallel ($S_0$) and perpendicular ($S_1$) to the
sample surface. Independently, the detector is also constrained using a slit. However, here we assume a symmetric constraint ($S_2$). In-plane diffraction geometry has the entire incoming beam illuminating the sample, but the detector slit reduces the area imaged on the surface. Figure 5.5(a) shows the changing active area observed on the sample. Consequently, diffraction peaks with low detector angles have a larger active area, while diffraction peaks with larger detector angles of diffraction have less active area. The reduction in active area reduces the observed intensity of diffraction peaks with greater detector angles. Therefore, in-plane diffraction data should be corrected in order to have intensities from all peaks on the same absolute scale.

$\alpha$-fixed mode

![Diagram](image)

Figure 5.6: This figure shows different orientations for $\alpha$-fixed scattering geometry. The initial frame shows the incoming and outgoing beams with the same angles ($\alpha = \beta$). The detector slit limits the observed range in $Q_\perp$, as indicated by the dashed box. The second frame shows the same incoming angle ($\alpha$) but an increased outgoing angle ($\beta$). In this geometry the range of integration along $Q_\perp$ has changed, reducing the total amount of intensity collected by the detector.

The $\alpha$-fixed geometry scans surface crystal truncation rods by keeping the incoming angle fixed while varying the outgoing angle, as shown in Fig 5.6. The figure shows an initial
orientation where the incoming and outgoing angles, Fig. 5.6(a), are the same. The detector slit width ($S_2$) results in an integration length along the rod indicated by the dashed rectangle. Larger out-of-plane scattering is obtained by rotating the sample and out-going angle ($\beta'$), as shown in Fig. 5.6(b). This geometry has the advantage of keeping the area illuminated by the incoming beam fixed. However, the active area observed on the sample is reduced, because the sample must rotate in order to observe the truncation rod. Also, increasing the out-going angle reduces the length of integration along the truncation rod, indicated by the dotted box in Fig. 5.6(b). Both corrections must be taken into account when using $\alpha$-fixed geometry for obtaining surface truncation rod information [29, 30].

$\beta$-fixed mode

![Diagram](image)

Figure 5.7: This figure shows different orientations for $\beta$-fixed scattering geometry. The initial frame shows the incoming and outgoing beams with the same angles ($\alpha = \beta$). The detector slit limits the observed range in $Q_\perp$, as indicated by the dashed box. The second frame shows the same outgoing angle ($\beta$) but an increased incoming angle ($\alpha$). In this geometry the range of integration along $Q_\perp$ has remained constant.

The $\beta$-fixed geometry is an alternative to the $\alpha$-fixed geometry, where the out-going angle ($\beta$) is held fixed while the incoming angle ($\alpha$) varies. Figure 5.7 shows the $\beta$-fixed ori-
entation for rod scattering where the out-going angle and the incoming angle are initially the same. Figure 5.7(b) shows the orientation to observe different positions along the rod, while keeping the out-going angle fixed. This geometry has the advantage of keeping the length of integration along the rod constant, as indicated by the same dashed rectangles in the two different panels. However, the changing incoming angle reduces the sample area illuminated by the incoming beam.

Using non-symmetric slits in $\beta$-fixed mode can increase the observed intensity from the sample. Not using a perpendicular detector slit allows for a larger integration range along the rod. The increased rod integration increases the total intensity collected from the surface, which is useful when the diffraction peak is weak. Therefore, changing the scattering geometry, during an experiment, can improve data collection, once the geometry corrections are understood.

5.3.2 Geometry Correction Calculations

The geometrical corrections applied to experimental data depend on the reciprocal space condition during each scan. The corrected data can be modeled and compared with data, independent of the diffractometer condition used. There are four different geometrical corrections: Lorentz, Polarization, resolution, and active area. The data collected in this thesis used a Psi-circle diffractometer [45]. However, here we will assume a six-circle diffractometer geometry [30]. The diffractometer geometry relates to the general scattering geometry angles shown in Fig. 3.1:
\[\alpha = \theta_i \quad \beta = \theta_f \]
\[\omega = \phi_i \quad \delta = \phi_i + \phi_f \]

(5.1)

**Rod Scattering Corrections**

Transverse scans for rod scattering data involve in-plane and out-of-plane components to be considered. The corrections use (H,K,L) values taken from data log files, like the example in appendix B. The reciprocal space values are used to calculate diffraction angles in eqn. 5.1. The polarization, active area, and Lorentz factors are then calculated, based on the diffraction angles. Finally, the corrections are applied to the Integrated Intensities taken from transverse scans for each peak, as shown in the previous section.

The corrections can be applied to the observed integrated intensities to obtain the "true" integrated intensities by the following convention:

\[I = I(\text{obs}) \frac{\text{Lorentz} \ast S_1 \ast S_2}{\text{Resolution} \ast \text{Polarization} \ast \text{Area}}\]

(5.2)

The first step is to calculate the angles based on reciprocal space condition, from eqn. 3.1. The wave vectors \((\vec{k}_i, \vec{k}_f)\) are separated into their parallel and perpendicular components, which are then used to calculate the angles:
\[
\frac{L}{c} = \sin(\alpha) + \sin(\beta) \quad \text{(a)}
\]

\[
\cos(\delta) = \frac{\cos^2(\alpha) + \cos^2(\beta) - \lambda^2 \frac{(h^2 + k^2 + l^2)}{a^2}}{2 \cos(\alpha) \cos(\beta)} \quad \text{(b)} \quad (5.3)
\]

The calculations work for both \(\alpha\)-fixed and \(\beta\)-fixed geometries. When using \(\alpha\)-fixed geometry, the \(\alpha\) is a constant value fixed during the experiment. For example, a rod scanned with fixed \(\alpha = 0.1^\circ\) results in a changing \(\beta\) calculated using eqn. 5.3(a). Once \(\alpha\) and \(\beta\) are determined, the detector angle (\(\delta\)) is calculated using eqn. 5.3(b). Using the same equations for \(\beta\)-fixed mode, a changing \(\alpha\) and \(\delta\) can be calculated. Thus, integrated intensities can be corrected independent of the scattering used.

The next step is to calculate the polarization correction factor. The 6IDC beam line at the Advanced Photon Source uses a linearly polarized beam, where the direction of polarization aligned horizontally. In this thesis, the sample is aligned so the direction of linear polarization is perpendicular to the sample surface. Conveniently, the perpendicular polarization geometry is worked out by others [30, 31]:

\[
\text{Polarization} = 1 - \left[ \sin(\alpha) \cos(\beta) \cos(\delta) + \cos(\alpha) \sin(\beta) \right]^2 \quad (5.4)
\]

The next step is to calculate the active area correction. Based on the active area geometry of section 5.3.1, there are three regions of corrections:
\[
\sin(\alpha_1) = \frac{S_0}{\text{sample size}} \quad \text{Beam Spill-off (a)}
\]

\[
\sin(\alpha_2) = \frac{S_0}{[S_2 + S_1 \cos(\delta)]} \cdot \sin(\delta) \quad \text{Active Area (b)} \quad (5.5)
\]

\[
\sin(\alpha_3) = \frac{S_0}{[S_2 - S_1 \cos(\delta)]} \cdot \sin(\delta) \quad \text{Reduced Active Area (c)}
\]

where the in-plane slit widths \((S_1, S_2)\) are given in Fig. 5.5, and the slit \((S_0)\) is the beam width perpendicular to the sample surface.

Instead of using the angles, the applied corrections use the experimental L-value to determine the active area region. Because, the data is given in terms of reciprocal lattice units, the angles for each active area region must be converted to L-values. First, the corresponding L-value is calculated for each region \((\alpha_1, \alpha_2, \alpha_3)\) using eqn. 5.5. Then, the L-value, of the transverse scan, is compared to the calculated L-value for each active area region. Finally, the appropriate area correction is applied. However, there are two special active area cases to consider:

(I) If the sample is smaller than the viewable detector area then
the active area will always be greater than the size of the sample.

\[
\text{Area} = \frac{S_1 + S_2}{\sin(\delta) - w^2 \tan(\delta)} \cdot \frac{d_{\text{sample}}}{2.0}
\]

\[
w \equiv \frac{(S_2 + S_1 \cos(\delta))}{2.0 \sin(\delta)} - \frac{d_{\text{sample}}}{2.0}
\]

(II) If the sample is small and \(\beta\) is fixed so that the reduced active area region is never observed

\[
\text{Area} = S_1 \cdot d_{\text{sample}}
\]

where both corrections are applied for all \((H, K, L)\) positions.

If the scattering geometry does not fall within the special cases, then one of the three
active area corrections are applied:

<table>
<thead>
<tr>
<th>Region</th>
<th>Area Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) Spill-off Region</td>
<td>$\text{Area} = \frac{S_1 \cdot S_2}{\sin(\delta)}$</td>
</tr>
<tr>
<td>(II) Active Area Region</td>
<td>$\text{Area} = \frac{S_1 \cdot S_2}{\sin(\delta)} - x^2 \cdot \tan(\delta)$</td>
</tr>
<tr>
<td>(III) Reduced Area Region</td>
<td>$\text{Area} = \frac{S_1 \cdot S_0}{\sin(\alpha)}$</td>
</tr>
</tbody>
</table>

The Lorentz factor is calculated for the given geometry [30, 31]:

\[
\text{Lorentz} = \sin(\delta) \cos(\alpha) \cos(\beta) \quad (5.6)
\]

Finally, a resolution correction is required to account for the reduction of slit integration. The $\alpha/\beta$-fixed sections outlined how the integration of the rod changes with increasing exit angle ($\beta$). The reduced length of integration is then:

\[
\text{Resolution} = \cos(\beta) \quad (5.7)
\]

**Geometry Correction Applied to $\alpha$-phase Rod Scattering**

The $\alpha$-phase ($\frac{2}{3}, \frac{2}{3}, L$) rod can be used to compare the geometry corrections for $\alpha$-fixed and $\beta$-fixed scan modes. Because, the $\alpha$-phase is a single layer on the Si(111) surface, the resulting ($\frac{2}{3}, \frac{2}{3}, L$) rod intensity will smoothly vary as a function of $L$. If the scattering rod had strong scattering from multiple layers, then any variation in rod intensity may result from both geometrical factors and layer interactions. Consequently, comparing geometrical corrections for $\alpha$-fixed and $\beta$-fixed scans, for a rod with multiple layers, would not be an ideal test; improper geometry correction, between scan modes, would be convoluted with
possible layer deviations. Therefore, the \((\frac{2}{3}, \frac{2}{3}, L)\) rod provides an ideal example to compare \(\alpha\)-fixed and \(\beta\)-fixed mode corrections, without any multi-layer scattering contributions.

Figure 5.8: This figure shows rod scans of the \(\alpha\)-phase \((\frac{2}{3}, \frac{2}{3}, L)\) rod using both \(\alpha\)-fixed and \(\beta\)-fixed modes. The \(\alpha\)-phase was prepared by annealing the 1.2ML Pb/Si(111)7x7 wetting layer to 300°C and quenched to -45°C. The top panel shows the uncorrected integrated intensity for the two modes. The data were scaled to the same intensity at \(L=0.1\) rlu. The \(\alpha\)-fixed data was collected with \((S_1 = S_2 = 1mm)\), whereas the \(\beta\)-fixed data had \((S_1 = 1mm, S_2 = 20mm)\). The bottom panel shows the data corrected for their respective scattering geometries using the methods outlined in section 5.3.2. The corrected data were scaled to the same starting intensity of the uncorrected data. The figure shows that the corrected \(\alpha\)-fixed and \(\beta\)-fixed mode data sets overlap, unlike the uncorrected data. Therefore, the geometry corrections provide rod scattering data independent of instrumental effects.

Figure 5.8 shows that the uncorrected integrated intensity of the \((\frac{2}{3}, \frac{2}{3}, L)\) is drastically different for \(\alpha\)-fixed and \(\beta\)-fixed modes. The \(\beta\)-fixed mode data decreases more rapidly, with increased \(L\)-value, than for the \(\alpha\)-fixed mode. The \(\beta\)-fixed mode intensity reduction is dominated by the active area. The reduced active area, described in section 5.3.1, is dependent on the incoming angle \(\alpha\). Consequently, the active area is constant in \(\alpha\)-fixed
mode, whereas the area changes with $\beta$-fixed mode. Moreover, the reduced active area correction dominates other corrections. Therefore, the $(\frac{2}{3}, \frac{2}{3}, L)$ rod example shows the importance of instrumental effects on experimental data.

Figure 5.8 also shows that geometry corrected rod data results in the same integrated intensity of $(\frac{2}{3}, \frac{2}{3}, L)$ rod scanned with $\alpha$-fixed and $\beta$-fixed modes. The corrected data, in the bottom panel, shows the same intensity versus $L$ for the different modes. The data in the top panel were corrected using eqn. 5.2. Also, the data were scaled to the same intensity value $L=0.1$ of the uncorrected data. Therefore, the comparison of $\alpha$-fixed and $\beta$-fixed modes, for the $(\frac{2}{3}, \frac{2}{3}, L)$ rod, provides confidence that resulting integrated intensity can be modeled independent of scattering geometry.

**In-plane Corrections**

The in-plane diffraction data is a subset of rod scattering, with a fixed $L$-value. Consequently, the diffraction data is corrected for the same factors described in the previous section at a fixed $L$-value. At fixed $L$ the incoming and outgoing angles $(\alpha, \beta)$ are constant and small so only the in-plane angles change $(\delta)$. Therefore, the geometrical corrections in eqn. 5.2 result in a scale factor with only in-plane angle variation:

$$I = I_{\text{obs}} \times \text{const.} \times \sin^2(\delta) \quad (5.8)$$

Detector slits may be different for in-plane diffraction and rod scattering, and the scale factor above explicitly accounts for the difference. In-plane diffraction data are usually obtained at a fixed $L$-value with open detector slits along the perpendicular direction. Rod
scattering data has different slit sizes depending on the scattering mode. $\alpha$-fixed mode has closed slits, whereas $\beta$-fixed has open slits along the perpendicular direction. Consequently, either the rod or in-plane data must be scaled to account for the slit difference. In this dissertation, the rod integrated intensity data were scaled, so the $L=0.1$ for each rod equal the peak obtained from in-plane diffraction.

**Transverse Scans**

![Transverse Scan](image)

Figure 5.9: This figure shows a typical transverse scan of a diffraction peak. The scan was taken from a reflectivity scan of the Pb/Si(111)7x7 surface at $L=1.2$ rlu. The figure shows the intensity of a diffraction peak as a function of transverse angle. The angle ($\mu$) relates to the incoming beam out-of-plane angle ($\theta_i$) in Fig. 3.1. The transverse scan has both Bragg and diffuse components. The Bragg component (Red dotted line) is fit using a Gaussian line shape. The diffuse component (Green Long dashed line) is fit using a Lorentzian line shape.

Theoretical models assume perfect correlation in an infinite crystal resulting in sharp diffraction peaks which experimentally observed diffraction peaks don’t have, due to effects such
as small surface order or a non-monochrome incoming beam. However, finite peak width effects can be overcome by collecting all of the scattered intensity from a diffraction peak using a transverse scan at each peak, as shown in Fig. 5.9. The transverse scan rotates the crystal through an angular range larger than the width of the peak to accurately distinguish background scattering. The transverse scan is used in all geometries to obtain true scattering intensity from the crystal. For in-plane diffraction and rod scattering geometries, the transverse angle ($\mu$) relates to the in-plane sample angle ($\phi_i$). For reflectivity, the transverse angle ($\mu$) relates to the in-plane sample angle ($\theta_i$).

**Peak Shape**

The shape of transverse diffraction peak has both specular and diffuse components. Figure 5.9 shows transverse intensity profile from a reflectivity scan on a Pb/Si(111)7x7 surface. The peak was fit using two Gaussian curves, as shown in the figure. Fitting the peak allows for a quantitative determination of the integrated intensity for the specular and diffuse components, independent of background scattering. Furthermore, following the specular and diffuse components can provide information about disorder and surface domain sizes, as described below.
5.3.3 Specular/Diffuse Contributions in Reflectivity

Figure 5.10: This figure shows the reflectivity of a Pb/Si(111)7x7 surface, along with the separate specular and diffuse contributions. The surface was obtained by depositing 1.1ML at 40°C followed by a quench to -45°C. The specular and diffuse contributions were determined from fits to the transverse scans taken at each data point. The combined reflectivity profile shows a smoothly varying intensity with the bulk Si(111) Bragg peak at L=3. Also, a smaller Pb(111) Bragg peak is observed as L~3.25. Plotting the separate specular and diffuse contributions shows that the Pb(111) Bragg peak only exists in the diffuse contribution. Therefore, the Pb(111) Bragg peak results from randomly oriented islands on the surface.

Diffuse scattering can determine interface structures not directly correlated with the surface, such as randomly oriented crystals, that can prevent accurate modeling of the surface. Figure 5.10 shows specular and diffuse contributions to reflectivity from the Pb/Si(111)7x7 interface, determined by transverse scans of the surface. The combined reflectivity from the interface shows a smoothly varying intensity with a sharp bulk-Si(111) Bragg peak at
L=3 followed by a smaller peak at L=3.25, which is the position of bulk-Pb(111) Bragg diffraction. When the combined reflectivity is separated into specular and diffuse components, the smaller peak contribution comes entirely from diffuse scattering. The diffuse scattering indicates that the contribution from bulk Pb(111) results from Pb-crystals which are not well ordered on the surface, and is consistent with known Pb-crystallite formation in the Pb/Si(111) system. Transverse scans near the bulk Pb(111) position are shown in Fig. 5.11. The scans show the increase in diffuse scattering. Therefore, separating out the specular and diffuse components of scattering is important to determine whether surface contributions are well ordered with the substrate or result from less ordered structures.
Figure 5.11: This figure shows the transverse scans for the reflectivity of a Pb/Si(111)7×7 surface in Fig. 5.10. The transverse scans show an increase in diffuse scattering contribution near $L=3.3$, resulting from initial formation of bulk Pb(111) crystals.
5.3.4 In-plane Domain Size Determination

Figure 5.12: This figure shows the total transverse width of diffraction peaks, for the clean Si(111)7x7 surface, as a function of lattice spacing ($d_{hkl}$). The transverse width was determined by fitting the transverse width of each in-plane diffraction peak, similar to fig. 5.9. The lattice constant ($d_{hkl}$) was calculated from the reciprocal space diffraction peak to real-space relationship eqn. 4.6. The Debye-Sherrer equation 5.9 shows that the transverse domain size is $\approx 6000(\pm1000)$ Å.

Transverse width of surface diffraction peaks can also determine the domain size for reconstructions on the surface, as shown in Fig. 5.12. The figure shows the full width at half maximum (FWHM) versus correlation lengths for the clean Si(111)7x7 reconstructed surface. When domain size contributions dominate the transverse width, the width will increase linearly with correlation length. The Debye-Sherrer equation, eqn. 5.9, describes the relationship of domain size (L) as a function of reciprocal space. The slope of the line indicates the domain size on the surface, as indicated in the figure. Thus, the average Si(111)7x7 domain size, created using our preparation method, is approximately $\approx 6000(\pm1000)$ Å. Therefore, transverse width provides an easy and effect method for surface
domain size determination.

\[ L = \frac{\lambda}{\sin(\theta)\Delta(2\theta)} \propto \frac{d_{hkl}}{\Delta \omega} \]  

(5.9)

5.3.5 Experimental Data Collection

Beamline Data Files

The files created during experimentation set the basis for all analysis software used during modeling. An example of a log file scan is given in appendix B. The header markers are used to choose the scan files and columns for data analysis: the #S header marks the scan number for reading, and is used to find scans using software; the #L marker indicates what columns correspond to the different detector channels, and the software is manually coded to pick the monitor and detector columns; the #R marker indicates SPEC-software determined values for the scan, such as peak intensity and peak width. The log file stores all the raw data information necessary for any experimental data analysis.

An experimental scan-log file is created during in-plane, reflectivity, and rod scans which store additional analysis for each scan, such as reciprocal space (H,K,L) position and absorber number used. An example data-log file is given in appendix B, which shows a typical file for in-plane diffraction scans. The analysis uses the column information to create directories, search the SPEC-log for scans, as well as other important steps.

5.3.6 Data Analysis Software Procedure

The data analysis software follows five different steps using two unique C-plot macro files. The macros are designed to run within the C-plot environment. The data analysis procedure is similar for Reflectivity, in-plane diffraction, and rod scattering. Each type of scan
has a data-log file, similar to the file in appendix B, and the software adjust depending on the number of columns in the data-log file (i.e. HKL-columns, or just L for reflectivity). The data analysis files all have similar names (stage1_v3.plt, rod-stage1_mac.plt, ref-stage1_mac.plt).

The first step is to copy the SPEC-log, data-log, stage1_v3.plt, and step1_v3.plt files into a manually created directory. The SPEC-log file should be named "log.log" and the data-log file should be named "data-log.dat." The second step is to run the Stage1_v3.plt file in the C-plot environment. The third step is to review the initial peak data and final fit peak data in C-plot. The fourth step is to review the 2D diffraction map created using Step1_v3.plt. The final step is to manually correct any peaks which were not fit properly. These steps are the general process for in-plane, rod scattering, and reflectivity data analysis software.

Stage1_v3.plt The first software to be run is called Stage1_v3.plt. This program initially creates all the subroutines that will be used in the fitting:

[1] plot.plt: This file is a generic plot file that takes the scan# and peak positions as inputs. It prints the transverse scan data to the screen, and saves it to the directory.

[2] fit_pks.plt: This file is the subroutine to fit the individual transverse scans. It assumes that fit_pks2.5 fit function is loaded into C-plot memory. This program takes the peak position, FWHM, data file, and limits of fitting as inputs. This program has the hard coded assumptions of the peaks (e.g. the second peak intensity is approximately 3.314 times the first peak intensity, see pks_2.5 fit function for more info) and must be re-written for different Metal/Semiconductor systems. The function outputs the parameter file and fit profile.
for the peak.

[3] **stage2_mac.awk**: This function creates a 'stage1_mac.plt' C-plot file which runs the 'fit_pks.plt' fit routine for each transverse scan. It provides all the information to the fitting routine, such as peak position and data directory.

[4] **stage3_mac.awk**: This function creates the 'stage3_mac.plt' C-plot file which plots all the transverse peaks, after they have been fit, to show the quality of fit to the data.

[5] **int_plot.awk**: This function creates the 'int_plot.plt' C-plot file which plots all the initial transverse scans, and creates the initial data for fitting.

[6] **mkdir.awk**: This file creates a 'mkdir.unx' unix command line file, which creates all the data directories for storing transverse data and fitting information.

**Step1_v3.plt**

The second program 'step1_v3.plt' is called by 'stage1_v3.plt' and creates a diffraction plot to view all transverse scans on a single figure. The

[1] **prm.exe**: This subroutine scans through the parameter files created by fitting in stage2_mac.plt. The routine outputs the fit area of each peak and the $\chi^2$ value for the fit.
[2] **datafind.awk**: This routine runs the prm.exe subroutine for each peak in the data-log.dat log file. The routine outputs the data into a file called 'amplitude_data.dat' file.

[3] **awk_rotate.bat**: This subroutine takes the 'amplitude_data.dat' file and maps the h,k columns onto a hexagonal unit system. This will allow C-plot to create a hexagonal plot on its cubic axis. The routine outputs the data into a 'rotation_data.rot' file.

[4] **awk_symbol.bat**: This subroutine takes each peak from the 'rotation_data.rot' file and creates three lines that tell C-plot to make circle symbols, with area of symbol proportional to the integrated intensity of the peak. This routine outputs the data to a file called 'symbol_data.plt'.

[5] **data.plt**: This file is a macro command to set the C-plot axis, and calls the 'symbol_data.plt' file to plot the data on an 'area plot'.

[6] **rename.bat**: This final routine takes the 'amplitude_data.dat' file and creates a four column raw data file for manipulation and model fitting. The output file is called 'rename_me.dat' and is meant for you to rename the file.

### 5.3.7 Error Analysis of Diffraction Data

The uncertainty in diffraction data must account for systematic errors as well as statistical errors, caused by diffractometer misalignment and sample preparation and surface degra-
dation. The systematic errors can be obtained by taking advantage of the surface symmetry to determine variations on diffraction peaks [24]. If a collection of diffraction peaks were obtained, then all of the symmetry equivalent peaks in the set could be averaged down to a minimum set of intensities and errors. Subsequently, the systematic errors could be used to determine if an adsorbed over layer breaks the symmetry of the substrate [33], by collecting the same data set before and after deposition.

First, the weighted average for the integrated intensity and statistical error for each peak is calculated:

$$\tilde{I} = \frac{\sum_{j=1}^{n} I_j}{\sum_{j=1}^{n} \sigma_j^2}$$ \hspace{1cm} \text{Weighted Intensity Average} \hspace{1cm} (5.10)

$$\tilde{\sigma} = \sqrt{\frac{\sum_{j=1}^{n} \frac{1}{\sigma_j^2}}{\sum_{j=1}^{n} \frac{1}{\sigma_j^2}}}$$ \hspace{1cm} \text{Weighted statistical Error}

$$s = \sqrt{\frac{\sum_{j=1}^{n} \frac{I_j^2}{\sigma_j^2} - \tilde{I}^2}{\sum_{j=1}^{n} \frac{1}{\sigma_j^2}}}$$ \hspace{1cm} \text{Standard Deviation}

Equation 5.10 shows how the weighted averages ($\tilde{I}, \tilde{\sigma}$) are obtained. The index for the averages (j) represents different symmetry equivalent peaks: if the intensity of the $\tilde{I}_1=\{(0,0), (0, \frac{g}{2}), (\frac{g}{2}, 0), \ldots \}$ peaks were all obtained, then the weighted average index would represent each symmetry equivalent peak and statistical error from the scans $\tilde{I}_1=\{j=1, j=2, j=3, \ldots \}$; a separate index for the $\tilde{I}_2=\{(\frac{g}{2}, 0), (0, \frac{g}{2}), (\frac{g}{2}, \frac{g}{2}), \ldots \}$ peaks would be used for their weighted intensity average. Subsequently the standard deviation (s) from the average would then be calculated for each set of symmetry equivalent peaks. Therefore, the resulting averages would provide a single symmetry inequivalent intensity, with a weighted statistical error and standard deviation, for each diffraction peak in the data set.

Second, the weighted averages can then be averaged to determine a total systematic and
experimental error:

\[
\epsilon = \frac{1}{N} \sum_{l_i \geq 20r} \tilde{I}_r \quad \text{Error of Symmetry} \quad (5.11)
\]

\[
\tilde{\sigma}'_r = (\tilde{\sigma}^2_r + \epsilon^2 \tilde{I}_r^2)^{1/2} \quad \text{Total Experimental Error} \quad (5.12)
\]

Each peak in the minimum data set obtained from weighted averaging has an index \(r\) used to determine the error of symmetry \(\epsilon\): if the averaged data set has \(X=\{(\frac{6}{7},0), (\frac{8}{7},0), (\frac{9}{7},0), \ldots\}\), then the index corresponds with each averaged peak \(X=\{	ilde{I}_1, \tilde{I}_2, \tilde{I}_3, \ldots\}\). The total experimental error for the diffraction data is then a quadrature summation of the statistical and systematic errors of the system. Subsequently, the error for any data set, in-plane diffraction or rod scattering, can be calculated using the symmetry method.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>(\frac{6}{7})</th>
<th>(\frac{8}{7})</th>
<th>(\frac{9}{7})</th>
</tr>
</thead>
<tbody>
<tr>
<td>((-\frac{n}{7}, \frac{n}{7}))</td>
<td>0.77</td>
<td>0.81</td>
<td>0.65</td>
</tr>
<tr>
<td>((0, \frac{n}{7}))</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>((\frac{n}{7}, 0))</td>
<td>1.26</td>
<td>1.12</td>
<td>1.12</td>
</tr>
<tr>
<td>((\frac{n}{7}, -\frac{n}{7}))</td>
<td>1.01</td>
<td>0.99</td>
<td>0.97</td>
</tr>
</tbody>
</table>

\(r=1,2,3\)

| \(I_r\) | 0.95 | 0.953 | 0.8537 |
| \(s_r\) | 0.168 | 0.115 | 0.191 |
| \(\epsilon\) | 0.174 |
| \(\tilde{\sigma}'_r\) | 0.172 | 0.172 | 0.155 |

Table 5.1: This table shows the \(p\text{6}mm\) symmetry equivalent intensity for three different in-plane diffraction peaks, normalized to the \((0, \frac{n}{7})\) symmetry peak. The Error analysis calculation results are shown for the data set.

The Pb/Si(111)\(7\times7\) in-plane diffraction data is a useful example to highlight the strength of the averaging technique. Table 5.1 shows an experimental data set for three different sets of diffraction peaks and their symmetry equivalent peaks. The data for each peak has been normalized to the \((0, \frac{n}{7})\) peak. The data was collected after \(\sim 1.1\text{ML}\) of Pb was deposited on
a Si(111)\textit{7}x\textit{7} surface at 40°C. The statistical error for each integrated intensity was <1%, highlighting that the data was limited by systematic errors. Each symmetry equivalent peak in the first set of columns results in the weighted averages in the second data table set. The weighted averages resulted in a single error of symmetry (ε). Finally, the total error for each peak is calculated in the final row.
Chapter 6

Experimental Results

Our structural analysis of the Pb/Si(111) system resulted in several surprising observations about the coverage-dependence and kinetics of the wetting layer. The coverage dependence of the Pb/Si(111)7x7 surface indicates that the wetting layer completes at \( \sim 1.1 \text{ML} \), followed by growth and coalescence of Pb-islands. The temperature and time dependence of the wetting layer, at 1.1ML coverage, shows an unexpected structural change over a temperature range of \( \sim 200^\circ \text{C} \); The surface increases structural order over time, when grown between 30°C and 150°C, while the surface reorders to a Pb/Si(111)1x1 structure when grown above 150°C. Also, the reordering to a Pb/Si(111)1x1 surface is accompanied by the formation of large bulk Pb-crystallites above 1ML coverage. The final structural analysis was done on a stable Pb/Si(111)7x7 wetting layer grown at 40°C and quenched to -45°C. X-ray reflectivity, in-plane diffraction, and rod scattering were used to determine the final structure.
6.1 Previous Pb/Si(111)7x7 Patterson Analysis

Figure 6.1: This figure shows an initial X-ray diffraction and Patterson analysis study of the Pb/Si(111)7x7 interface[8, 9]. (a) The in-plane diffraction pattern was obtained with 2.2ML Pb-coverage deposited on the clean Si(111)7x7 surface at 30°C. (b) The Patterson map was created using the in-plane diffraction and eqn3.12. The resulting map shows an 8x8 set of lattice spacings. However, contour lines around bond length positions quickly decreases with increasing distance, indicating the 8x8 order is not uniform through the entire unit cell.

Patterson analysis of Pb/Si(111)7x7 in-plane X-ray diffraction provided the initial structural model of the wetting layer [8, 9]. A large collection of in-plane diffraction peaks were obtained after 2ML of Pb-atoms were deposited on the clean Si(111)7x7 surface at room temperature, as shown in fig. 6.1(a). Subsequently, the integrated intensities were used as the Fourier coefficients in eq. 3.12(b), resulting in a Patterson Map shown in fig. 6.1(b). The map shows a 8x8 lattice of bond lengths. Furthermore, the 8x8 lattice follows the pseudo-symmetry of the 7x7, as indicated by the triangle.

Interpretation with Patterson Analysis limits the determination of a wetting layer model. As discussed in section 3.3.2, Patterson Analysis is biased by the strongest diffraction intensities. Consequently, the strong $(\frac{8}{7}, 0)_h$ in-plane diffraction peak biases the Patterson
Map to give predominantly 8x8 lattice spacing, and limits determining deviations from 8x8. Furthermore, the Patterson Map is a correlation function of electron density, and not a determination of real-space positions. Consequently, the strong contours near the corner of the unit cell suggest nearest-neighbor atoms are close to 8x8 lattice spacing, but the 8x8 correlation quickly deviates with increased lattice spacing. Furthermore, the strongest correlation is not necessarily near the corner of the unit cell, as the map suggests, but rather could also start from the center of the unit cell. Both positions of strongest correlation maintain the six fold symmetry and would result in the same Patterson Map. Therefore, the Patterson analysis on the surface determined the general structure of the wetting layer, but was limited in determining exact atomic positions on the surface.

The Patterson Analysis also indicates that the \((\frac{8}{7}, 0)_n\) in-plane diffraction peak provides the overall order of the wetting layer. If the wetting layer prefers the 8x8 order, then studying multiples of the \((\frac{8}{7}, 0)_n\) peak will provide information about the wetting layer. For example, if the wetting layer completes at 1ML Pb-coverage, then the \((\frac{8}{7}, 0)_n\) intensity will maximize with 1ML Pb-coverage on the surface. Therefore, in this thesis, the intensity of the \((\frac{8}{7}, 0)_n\) peak will be presented for different coverage-temperature conditions, to describe the order of the wetting layer.
6.2 Overall order of the Pb/Si(111)7x7 Structure

Figure 6.2: The coverage-dependence (Θ) of the \((\frac{8}{7}, 0)_H\) diffraction peak intensity at \(\sim 40^\circ C\). The clean Si(111)7x7 intensity starts at \(\sim 0.08\) before deposition. (a) The wetting layer completion is indicated by the maximum intensity of 5.0 at a Pb-coverage \(\sim 1.1\text{ML}\), followed by the formation of QSE islands at higher coverage. (b) This indicates that the previous X-ray diffraction analysis of the Pb/Si(111)7x7 interface, in the literature, was performed at a Pb-coverage where the wetting layer had already completed and partially transformed to islands \([8]\). (c) After the wetting layer has completed Pb-islands begin to form, and consume the wetting layer beneath them. (d) Islands begin to coalescence above \(\sim 10\text{ML}\) and layer-by-layer growth begins. Finally, once islands coalesce, the intensity decreases solely due to absorption of x-rays by the Pb-film. The adsorption can be modeled to estimate the ‘true’ intensity resulting from the Pb-island/Si(111)7x7 interface. The extrapolated arrow shows that the Pb-island/Si(111)7x7 intensity is \(\sim 0.2\) and suggests that the clean Si(111)7x7 surface is not entirely recovered beneath the Pb-islands.

Following the \((\frac{8}{7}, 0)_H\) diffraction intensity indicates the coverage dependence of the wetting layer, and would indicate which coverage to study the structure of the layer. Figure 6.2 shows the intensity of the \((\frac{8}{7}, 0)_H\) peak during Pb deposition. During deposition, the intensity peaks \(\sim 50\) times the starting clean surface intensity at \(\sim 1.1\text{ML}\), indicating the
completion of the wetting layer. Above 1.1ML Pb-islands begin to consume the wetting layer, which causes the intensity to decrease. Above \( \sim 10\)ML the islands coalesce and completely cover the surface. The decrease in intensity above 10ML is due to X-ray absorption by the over layer, and by extrapolating the intensity to 0ML coverage the correct interface diffraction intensity is obtained. The interface intensity below the coalesced surface shows that the clean Si(111)7x7 interface is not recovered when Pb-islands form on the surface.

The coverage-dependence of the intensity shows that the wetting layer structure should be studied at \( \sim 1.1\)ML. It is useful to note that previous X-ray diffraction studies in the literature were performed at 2.2ML [8, 9]. Above, \( \sim 1\)ML coverage, other X-ray studies show that QSE islands consume the wetting layer as they grow [2, 27]. This consumed wetting layer observation is further corroborated by the decreasing \((\frac{5}{7}, 0)_{\text{H}}\), which indicates decreasing the area of the surface covered by wetting layer, observed here. However, the fact that the clean Si(111)7x7 intensity is not recovered beneath the coalesced islands suggests that the island-substrate interface has been modified. Consequently, studying the diffraction of the Pb/Si(111)7x7 surface above 1ML would have contributions from both the wetting layer and the island/substrate interface, which may not be distinguishable.
6.3 Kinetic Instability of the Wetting Layer

Figure 6.3: This figure shows the time dependence of the $(\frac{8}{7}, 0)_H$ peak during deposition of $\sim 1.0$ML and for $\sim 30$min after deposition. Pb-atoms were deposited at a rate of $0.3 \pm 0.05$ML/min onto the clean Si(111)7x7 surface at 77°C, starting at $\sim 500$sec. The intensity continues to increase after deposition of a complete wetting layer, suggesting the wetting layer structure is changing after deposition.

Immediately following the deposition of $\sim 1$ML, the $(\frac{8}{7}, 0)_H$ peak showed an unexpected time evolution. Figure 6.3 shows the observed time dependence of the intensity during and directly following deposition. The sample temperature was held fixed at 77°C. Although intensity increases sharply from the initial clean Si(111)7x7 surface to a completed 1ML deposition, surprisingly, the intensity continues to increase after the shutter for the evaporator was closed. Consequently, the changing intensity could only result from a changing structure of the wetting layer. Therefore, it is necessary to understand how the wetting layer is changing before attempting to determine any steady state structure.

Following the time-dependence of the $(\frac{8}{7}, 0)_H$ intensity for different growth temperatures indicates the Pb/Si(111)7x7 interface is changing in two different ways. Figure 6.4 shows the intensity of the $(\frac{8}{7}, 0)_H$ peak as a function of time, after 1.2ML deposition. The intensity was normalized to the initial intensity just after deposition ($\sim 1$sec). When grown at 47°C or 77°C the intensity increases with time; furthermore, the rate of changing intensity increases with temperature. Contrastingly, the intensity decreases with time when
Figure 6.4: This figure shows the time-dependence of the peak intensity for the in-plane \((\frac{3}{2}, 0)_{H}\) peak. 1.2ML of Pb was deposited on the surface. The peak intensity is plotted versus elapsed time following the end of deposition, defined as 0 seconds. Each intensity is divided by the initial intensity obtained just after the deposition was stopped.

grown at 171°C or 198°C. Similar to the first regime, the rate of intensity change increases with increasing temperature, also.

The temperature range for each regime is distinguished by following the temperature dependence of the integrated intensity, taken immediately following deposition (~30sec). Figure 6.5 shows the changing integrated intensity as a function of growth temperature, as well as the transverse scan used to collect the data in the inset. The initial intensity increases with increasing growth temperature from -50°C to 150°C, indicated by the dotted dashed line. While above ~200°C the intensity begins to decrease, indicated by the dashed arrow. Therefore, the two different regimes of kinetic instability separate, and likely compete, around ~150°C. The wetting layer increases order \(\leq 150°C\), whereas the wetting layer decreases order \(\geq 150°C\).

The surprising dynamic behavior of the wetting layer shows that the wetting layer does not prefer its initial order, and that it prefers to order in two different ways. If the deposited
Figure 6.5: This figure shows the temperature dependence of the \((\frac{8}{7}, 0)_H\) integrated intensity. The \((\frac{8}{7}, 0)_H\) peak was scanned transversely, as shown in the inset, directly after deposition (~1min). The temperature of the sample during deposition is given on the x-axis, and the integrated intensity is given on the y-axis. The integrated intensity increases with sample temperature during deposition, until ~200°C when the integrated intensity begins to fall.

wetting layer were stable, then the diffraction intensity of the surface would be constant. Also, if the wetting layer were amorphous, then no diffraction intensity would be observed. However, following the changing intensity of the \((\frac{8}{7}, 0)_H\) peak alone does not completely explain how the structure of the wetting layer is changing. Consequently, the intensity of multiple \((\frac{8}{7}, \frac{m}{7})_H\) diffraction peaks should be studied for the two separate temperature regimes.
6.4 Increasing Order of the Wetting Layer With Annealing

![Graph showing intensity ratios of different diffraction peaks. The x-axis represents diffraction peaks, and the y-axis represents ratio integrated intensity. The graph shows two cases: during annealing at 100°C and after cooling to -45°C. The horizontal dashed line at a ratio of unity demarks the level of change: intensity ratios lower than unity indicate a weakening of the reflection, whereas ratios greater than unity indicate a strengthening. The intensity ratio for the \((\frac{15}{7}, 0)_H\) was rescaled because of its large change, skewing the other peaks.](image)

Figure 6.6: The intensity ratios of different diffraction peaks \((H,K,0.1)_H\), for a 1.2 ML Pb film are shown for two cases of annealing: one measured at the annealing temperature of 100°C (-1 hr.) and one measured after cooling to -45°C. The intensity ratio is defined as the intensity of the annealed wetting layer divided by the intensity of the as-deposited wetting layer at -45°C. The horizontal dashed line at a ratio of unity demarks the level of change: intensity ratios lower than unity indicates a reflection that weakens with annealing whereas ratios greater than unity indicates a strengthening of the reflection. Note that the intensity ratio for the \((\frac{15}{7}, 0)_H\) was rescaled because its large change skews the other peaks.

Following the diffraction intensity for different \((\frac{\ell}{7}, \frac{m}{7})\) peaks, during the annealing process, shows a changing atomic order within the wetting layer unit cell. The changing diffraction intensity was determined by plotting the ratio of intensities as shown in fig. 6.6. The dashed line, at a ratio of unity, indicates the level of change: intensity ratios greater than unity correspond with a reflection which strengthens, whereas ratios less than unity indicate a reflection that has weakened. The index for each peak can be easily visualized by using
the clean Si(111)7x7 diffraction map in Fig. 4.3 as a guide. Intensity ratios are greater than unity for the \((\frac{8}{7}, 0)\) and \((\frac{16}{7}, 0)\) during and after annealing the surface. Increased diffraction intensity indicates more atoms contribute to the scattering of the peak. Meaning, atoms are shifting toward sites which contribute to \((\frac{8}{7}, 0)\) and \((\frac{16}{7}, 0)\). Furthermore, peaks near the \((\frac{16}{7}, 0)\) also show an increase in intensity, whereas, ratios near \(\frac{8}{7}\) decrease with annealing. Therefore, Pb-atoms are transitioning toward a better ordered 8x8 structure for the wetting layer.

Figure 6.7: This figure shows the same increasing intensity data in Fig. 6.4 on a linear time-axis. The time is elapsed time after the deposition of 1.2ML. The fit lines to the data result from eqn. 6.1. The inset shows a plot of the resulting time constants \(\tau\) on an Arrhenius plot obtained from fits to the data, described in this section. The resulting fit to the time constants gives an energy barrier of \(0.4\pm0.2\) eV and attempt frequency \(\nu=2\times10^{(4\pm1)}\) Hz.

The temperature-dependence of the increasing \((\frac{8}{7}, 0)\) intensity after deposition can be analyzed using Arrhenius law to determine an energy barrier for the structural transition. Figure 6.7 shows the same two temperatures as in Fig. 6.4 on a linear time axis. The intensity for both temperatures asymptotically saturates. The data were fit using the exponential function:

\[
\frac{I}{I_0} = I_f(1 - e^{-\frac{t}{\tau}}) \tag{6.1}
\]

If the preferred wetting layer structure is an 8x8 lattice, then the intensity would stop
changing once all the Pb-atoms transition to 8x8 sites. Thus, the saturation intensity (I_f) corresponds to the wetting layer structure near an 8x8 steady state. The temperature-dependent time constant (τ) describes the rate at which the wetting layer will transition toward the 8x8 structure, for a given deposition temperature.

Arrhenius Law relates the temperature-dependent time constant with the energy barrier required for the structural transition:

\[ \tau = \nu \cdot e^{-E_b/k_B T} \]  
\[ \ln(\tau) = \ln(\nu) - \frac{E_b}{k_B T} \]  

(a) \hspace{1cm} (b) (6.2)

The attempt frequency (ν) represents the number of collisions per second occurring for the process. The energy barrier (E_b) represents the minimum energy required for the process to occur. Typically the log of the time constant plot versus \((\frac{1}{k_B T})\), as shown in eqn. 6.2(b). Subsequently, the relaxation constants can be fit to a line with slope equal to the energy barrier, and the intercept equal to the log of the attempt frequency.

The Arrhenius plot for the two increasing intensity time constants is given as an inset of fig. 6.7. The time constants, τ, from the single exponential fit were determined to be 600(±60) s at 47°C and 150(±15) s at 77°C. The linear fit through each time constant (solid line) indicates the energy barrier for the increasing intensity surface transition is 0.4±0.2 eV with an attempt frequency \(\nu=2\times10^{(4±1)}\) Hz. Because the Arrhenius analysis was limited to two deposition temperatures, the accuracy in the energy barrier was limited by systematic errors.

The measured energy barrier can be compared to various atomic-scale processes that have been discussed in the literature. For example, Pb adatom diffusion on the wetting
layer and on top of a QSE Pb island have barriers of 0.1eV and 0.05eV respectively [40]. These values are significantly smaller than the 0.4 eV barrier that we measured during the low-temperature annealing. However, rather than simple diffusion across a surface, our diffraction data in the low-temperature regime show that the Pb atoms rearrange within the unit cell, suggesting that the Pb atoms move in and out of the wetting layer. Indeed, LEEM studies have measured the barrier for Pb vacancy creation and annihilation in the wetting layer to be 0.36 eV and 0.2 eV, respectively [41]. This barrier is quite close to our measured value and this gives additional evidence that the low-temperature annealing observed in our experiment arises from an atomic-scale structural rearrangement of the wetting layer.
6.5 Decreasing Order of the Pb/Si(111)7x7 Structure with Annealing

Figure 6.8: The (8,0) peak intensity, normalized to $I_0$, measured as a function of elapsed time after 1.2ML of Pb was deposited at 210°C. The data exhibit a fast initial decay followed by a slower decay at longer time. The solid curve shows that eq. 6.3 which describes two exponential decay processes, provides a good fit to the data. Inset: Multiple in-plane (H,K)$_H$ reflections show approximately the same rate of intensity decay, indicating the loss of the 7x7 surface fraction with time.

The decaying intensity analysis indicates that the Pb/Si(111)7x7 surface reorders differently than for the increasing intensity process. Figure 6.8 shows the decaying intensity with elapsed time after the deposition of a 1.2ML at ~210°C. The intensity exhibits a fast decay rate for the first few minutes, followed by a much slower decay rate. The decaying intensity was fit using the two-exponential to match the two decay rates that are qualitatively observed in Fig. 6.8:

$$I(t) = I_1 e^{-\frac{t}{\tau_1}} + I_2 e^{-\frac{t}{\tau_2}}$$

(6.3)
Each exponential fits a single relaxation constant to each distinct portion of the decaying intensity. The pre-factor Ij’s (j=1,2) were found to be constant within ±10% for all deposition temperatures studied. Several different (π/7, mπ) peaks were also followed during the deposition, and the inset shows that they all exhibit the same decay rate, over a longer time period. Thus, the decaying Pb/Si(111)7x7 surface involves an entire unit cell breaking up, rather than re-ordering within the unit cell as had been observed for the increasing intensity process discussed in connection with Fig. 6.6. The time-dependent analysis therefore suggests that there are two separate decay rates (τ1, τ2) and that the reordering involves destroying the Si(111)7x7 reconstruction beneath the wetting layer.

Figure 6.9: ln(τ) for both time constants, τ1 and τ2, as a function of inverse temperature was obtained from fits of eq. 6.3 to the time decay of the (\( \frac{8}{7} \), 0)H intensity at different annealing temperatures. The τ’s are measured in seconds. The dashed lines represent fits to each set of time constants according to the Arrhenius behavior given in eq. 6.2.
Table 6.1: Activation energy, $E_b$, and attempt frequency, $\nu$, obtained from fitting eq.(6.3) to the data in Fig. 6.9.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
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</thead>
<tbody>
<tr>
<td>$E_b$</td>
<td>1.9 (±0.2) eV</td>
<td>1.3 (±0.2) eV</td>
</tr>
<tr>
<td>$\nu$</td>
<td>4(±0.5)x10^{17} Hz</td>
<td>6(±0.3)x10^8 Hz</td>
</tr>
</tbody>
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As with the increasing intensity analysis, energy barriers for the two decaying intensity processes can be determined from the temperature dependence of the relaxation constants. Figure 6.9 shows the natural log of each constant as a function of inverse temperature. The data show a linear relationship with inverse temperature, and are fit according to eq. 6.2. The energy barrier and attempt frequency for decay rate are given in table 6.1. The lower energy barrier corresponds to the longer time rate. While the Arrhenius analysis can provide an energy barrier for the transition, it does not provide an indication for any specific surface transition process each barrier is associated with. However, it is noted that the decay process involves the destruction of the 7x7 reconstruction, which would be expected to have a larger activation barrier than for the lower temperature increasing intensity process.
Figure 6.10: The decay of the \((\frac{5}{7}, 0)_{H}\) peak intensity with elapsed time after the deposition of a given coverage of Pb at 185°C. Note that the intensity decays more quickly for 1.5 ML than for 1.2 ML. There is no decay observed for 2.5ML. The solid curves are calculated from eq. 6.3 which was fit to the data. The inset shows the time constants vs. coverage for the fitted curves.

Our studies also reveal that the high-temperature decay of the Pb/Si(111)7x7 depends on the Pb coverage. Figure 6.10 shows the decaying \((\frac{5}{7}, 0)_{H}\) intensity with elapsed time for three different coverages that were deposited at 185°C. As can be seen, there is a marked increase in the decay rate in going from 1.2ML to 1.5ML coverage – this is quantitatively shown in the inset where the relaxation time decreases with coverage. In considering the 2.5 ML data in Fig. 6.10, it should be noted that the initial \((\frac{5}{7}, 0)_{H}\) intensity decreases with increasing coverage above 1.2 ML because the Pb nano-crystalline islands (see next section) consume the wetting layer directly below the islands and incorporate that Pb into the FCC structure of the islands, as has been reported elsewhere [1, 28]. Thus, the lower intensity for the 2.5 ML data in Fig. 6.10 is at least partly due to this effect. However, at a coverage of 2.5ML there is no discernable decay of the intensity with time at this temperature. Therefore, we cannot say whether the 2.5 ML data decays faster or slower than
the experimental measurement time, although, extending the trend from lower coverage would suggest that it decays faster, and has already decayed by the time it was measured. The result of Fig. 6.10 bears similarity to recent LEEM experiments on Pb/Si(111) [41] that have shown anomalous kinetic behavior of the Pb wetting layer in response to a hole generated by a short-pulsed laser. Those experiments showed that the Pb relaxation rate, $\frac{1}{\tau}$, increased with increasing coverage between 1.2-1.3ML with no change in relaxation rate at higher coverages. Some care in making a comparison between the two experiments should be exercised, however, since the activation energies differ by almost an order of magnitude. The higher activation energy in the present experiment is likely to be related to the motion of the Si adatoms that is required to remove the 7x7 reconstruction.

6.6 Structural Transition from Pb/Si(111)7x7 to Pb/Si(111)1x1

6.6.1 Temperature Dependence of 1ML $\alpha$-phase Ordering

The transition of the Pb/Si(111)7x7 surface at higher temperatures has been previously reported as a transition toward a collection of different Pb/Si(111)1x1 interface structures with complicated temperature and coverage dependence [36, 37, 38]. The collection of structural phases which exist above 1ML is called the $\alpha$-phase. Upon cooling our observed decayed surface we observed a diffraction peak associated with the $\alpha$-phase, as shown in fig. 6.11. The figure shows the intensity of a scan along a high symmetry direction, indicated in the inset, with a sharp peak near the expected position for an $\alpha$-phase interface. This indicates that the decaying intensity we observed in the previous section for the higher temperature anneal is due to the previously expected transition from Pb/Si(111)7x7
Figure 6.11: An [h,h]$_H$ scan shows that annealing 1 ML of Pb above 200°C and cooling to -70°C produces the main Bragg reflection of the $\alpha$-phase. Therefore the intensity decay observed in Fig. 6.4 relates to the destruction of the Pb/Si(111)7x7, which leads to the $\alpha$-phase upon cooling. The solid curve is a Gaussian and background that was fit to the data. The inset schematically shows the hexagonal reciprocal lattice with the direction of the scan.

to Pb/Si(111)1x1. The $\alpha$-phase forms once the sample is cooled below $\sim$50°C.

The annealing temperature of the Pb/Si(111)1x1 surface effects the overall order within the $\alpha$-phase. Figure 6.12 shows the annealing temperature dependence of the peak broadening and intensities of the $\alpha$-phase. The initial surface was prepared by depositing $\sim$1ML at 150°C and waiting until 95% of the Pb/Si(111)7x7 surface had transformed to Pb/Si(111)1x1. The data were collected by annealing the already created $\alpha$-phase to the listed temperature for $\sim$30min followed by a quench to -45°C. The surface was then scanned along the same direction in fig. 6.11 on the quenched surface. The intensity was fit using a single Gaussian with a sloping background. The peak broadening was determined by dividing the measured radial peak-width by the peak position.
The annealing studies show that the order of the $\alpha$-phase depends on the annealing temperature. The $\alpha$-phase consists of a collection of different phases [39] which create overlapping diffraction peaks near the same reciprocal space positions. Consequently, the breadth of the observed peak depends on the combination of domains. The decreasing peak width indicates that the $\alpha$-phase converges to a single structure with greater annealing temperature. The surface covered by $\alpha$-phase domains is determined by integrated intensity of the peak. The increasing integrated intensity indicates that the surface covered by $\alpha$-phase increases with annealing temperature. Therefore, the annealing-dependent analysis shows that removing the Pb/Si(111)7x7 isn’t enough to create an ordered $\alpha$-phase. The surface must be annealed to 300°C to create the best ordered $\alpha$-phase.
6.6.2 Coverage Dependence of $\alpha$-phase Ordering

Figure 6.13: This figure shows the intensity measured along the (h=k)-line $(a)$ before, $(b)$ during, and $(c)$ after annealing the 1.2ML Pb/Si(111)7x7 surface to 300°C. Before annealing, the scan shows a single $(\frac{5}{7}, \frac{5}{7})$ from the Pb/Si(111)7x7 surface. However, during an anneal to 300°C the $(\frac{5}{7}, \frac{5}{7})$ peak disappears, and two bulk Pb-crystallite peaks appear. After quenching the annealed surface to -10°C, the two Pb-crystallite peaks shift are obscured by the emergence of a strong $\alpha$-phase peak. The inset shows a transverse scan near $(0.67,0.67,0.1)$, indicating the existence of Pb-crystallite peaks.

Depositing more than 1ML on the surface results in the formation of bulk Pb-crystallites on the surface is indicated by fig. 6.13. The surface transition was studied by scanning along [H,H,0.1] before, during, and after annealing the surface to 300°C. The surface shows a single $(\frac{5}{7}, \frac{5}{7})$ peak corresponding to the Pb/Si(111)7x7 surface after deposition of 1.2ML at -10°C. The peak disappears when the surface is annealed to ~300°C, and two new peaks at $(0.667,0.667)$ and $(0.771,0.771)$ develop during annealing. The new peaks correspond to bulk Pb-crystallites on the surface. Upon cooling, the $\alpha$-phase forms in coexistence with the Pb-crystallites. The transverse scan at the $(0.667,0.667)$ position shows the Pb-crystallites remain after the annealing process. Furthermore, the sharp and random collection of peaks in the transverse scan shows that the Pb-crystallites are large and randomly oriented on the surface.
Figure 6.14: This figure shows two-dimensional imaging of the Pb-crystallite peaks. The area detector was positioned with the central bottom pixel of the camera at $2\theta \sim 21.8^\circ$. Images were taken while the crystal surface was rotated, and the detector held fixed. The surface was scanned with 1.2ML at $\sim 200^\circ$C. The observed rings are a collection of sharp diffraction peaks. The $2\theta$ values indicate where each ring intersects the sample horizon. The rings are indexed as $20.15^\circ$=$\text{Pb}(111)_{C}$ and $23.3^\circ$=$\text{Pb}(200)_{C}$ bulk powder rings.

The sharp peaks observed in transverse scans near $(0.667,0.667)$ and $(0.771,0.771)$ were also studied using an area detector. If one of the observed peaks along the transverse scan, near $(0.667,0.667)$, correspond to a surface layer, then a continuous rod of scattering would be observed. Using an area detector would easily show if any of the observed peaks exhibit continuous rod scattering. Figure 6.14 shows area detector scans of the observed crystallites in fig. 6.13. The images were obtained by holding the detector fixed at $2\theta \sim 21.8^\circ$ while rotating the sample at $\sim 200^\circ$C. The image shows rings, similar to powder diffraction, of sharp diffraction spots from a sparse population of randomly oriented crystals. The rings of diffraction were fit and indexed, correcting for the geometry of scattering, as shown in the right.
The observation of Pb-crystallites without continuous rod scattering accounts for uncertainty of previous $\alpha$-phase diffraction studies in the literature \cite{8, 9}. Previous grazing incidence X-ray diffraction showed two equally intense satellite peaks near the $(0.65,0.65)$ $\alpha$-phase diffraction peak, as discussed in section 2.3.3. The satellite peaks were assumed to result from domain walls within the $\alpha$-phase. However, the current observation shows that the location and random nature of the peaks correspond with randomly oriented Pb-crystallites on the surface. Furthermore, no continuous scattering rods are observed near the crystallite $2\theta$ positions.

![Figure 6.15](image)

Figure 6.15: This figure shows the Pb-coverage dependence of the $\alpha$-phase and Pb-crystallites. The Pb coverage is measured in units of bulk Pb-layers. The integrated intensities were taken from transverse scans, while the $\alpha$-phase positions were taken from radial scans along [h,h,0.1]. The integrated intensities of the $\alpha$-phase and Pb-crystallites both increase with Pb-coverage on the surface. However, the $\alpha$-phase intensity saturates at $\sim$1.2ML Pb-coverage, while the Pb-crystallite continue to increase. The radial peak position of the $\alpha$-phase peak also increases with coverage. The lines through the data are guides to the eye.

The coverage dependence of the $\alpha$-phase and Pb-crystallites were studied, as shown in fig. 6.15. The surface preparation occurred in two different ways. The 1ML surface was
prepared by annealing the 1ML Pb/Si(111)7x7 surface to 300°C. Below 1ML, the previously prepared 1ML α-phase was annealed above 350°C to desorb Pb from the surface. Pb coverage above 1.2ML was prepared by adding Pb onto the α-phase surface and annealing to 300°C. The integrated intensities were determined by integrating transverse scans for the α-phase and Pb[111]C positions. Also, the radial position of the α-phase diffraction peak along the h=k symmetry line is given as a function of coverage. The position of the α-phase peak was taken from fits to the data.

The integrated intensities show that the α-phase order increases on the surface up to 1ML. Above 1ML, Pb-crystallites begin to form. The location of the α-phase peak shifts with coverage. It is known that a collection of degenerate Pb/Si(111)1x1 structures exist, as presented in section 2.3.3, and each have a different atomic order. Therefore, the shifting peak position results from the order and proportion of degenerate surface structures.

### 6.7 Structural Determination of Stable Pb/Si(111)7x7 Wetting Layer

Now that the kinetics of the wetting layer are understood, we are in a position to investigate the crystal structure of the stable Pb/Si(111)7x7 wetting layer. The stable surface was prepared by depositing 1.1ML on the Si(111)7x7 at 40°C, followed by a quench to -45°C. The quenched surface was scanned using reflectivity, in-plane diffraction, and rod scattering geometry.
6.7.1 Reflectivity

We measured specular reflectivity of both the clean Si(111)7x7 and Pb/Si(111)7x7 surfaces to obtain average layer height and atomic density. Specular reflectivity is insensitive to in-plane atomic ordering, which simplifies the structural problem. We first measured the clean Si(111)7x7 reflectivity to obtain the initial position and density for the Si 7x7 surface reconstruction. Subsequently, we measured the Pb/Si(111)7x7 to obtain the wetting layer height and density. The resulting parameters provide initial values used to fit in-plane diffraction and rod scattering used later.
Figure 6.16: This figure shows the specular reflectivity of the clean Si(111)7x7 and 1.1ML Pb/Si(111)7x7 surfaces. The clean Si(111)7x7 data oscillates at higher L-values due to the three Si-layers (layer-1b, layer-1a, Ad-layer) as shown by the model fit (short dashed line) to the data. The Pb/Si(111)7x7 reflectivity is dominated by Pb-scattering from a single dense wetting layer, and shows a smoothly varying intensity compared to the clean Si(111)7x7. The Pb/Si(111)7x7 model fit (solid line) is for a single 0.9±0.1ML Pb-wetting layer sitting 2.6±0.1Å above the Si-1a layer, and includes the STM proposed Pb-adatom layer. Removing the Pb-adatom layer (long dashed line) does not qualitatively change the fit to the Pb/Si(111)7x7.

Figure 6.16 shows the measured reflectivity for the clean Si(111)7x7, with model fits from section 4.2, as well as the Pb/Si(111)7x7 surface. In modeling the data, we found the Si layer height and density values identical to previous X-ray scattering studies of the Si(111)7x7 [18], and are given in section 4.2. Our sensitivity in layer height for layers Si-1a and Si-1b were both determined to be ±0.2Å, and ±0.5Å for the adatom-layer. Sensitivity to the adatom layer is less than layer-1a or layer-1b, because the adatom layer density
is significantly less, than the other layers. The vertical positions and layer densities obtained from the Si(111)7x7 reflectivity were used for the initial values in the Pb/Si(111)7x7 analysis.

The smoothly varying reflectivity of the Pb/Si(111)7x7 surface is strikingly different than for the clean Si(111)7x7 reflectivity. Pb atoms are stronger scatterers of X-rays than Si atoms, which means that the Pb/Si(111)7x7 reflectivity will be dominated by the Pb scattering. The smoothly varying intensity suggests that the reflectivity results from a single Pb-layer on the surface. A reconstruction with multiple equally dense Pb layers would result in an oscillatory reflectivity, as is observed for the clean Si(111)7x7 data. The model fit will be involve the majority of Pb atoms in a single dense wetting layer.

<table>
<thead>
<tr>
<th>Layers</th>
<th># of Atoms</th>
<th>Δz (Å)</th>
<th>σz (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb Wetting Layer</td>
<td>53(6)</td>
<td>2.65(0.2)</td>
<td>0.2(0.1)</td>
</tr>
<tr>
<td>Pb-adatom Layer</td>
<td>6(6)</td>
<td>2.1(0.2)</td>
<td>0.1(0.1)</td>
</tr>
<tr>
<td>Adatom Layer</td>
<td>12(12)</td>
<td>0.88(0.5)</td>
<td>0.0(0.1)</td>
</tr>
<tr>
<td>layer-1a</td>
<td>42(4)</td>
<td>0.0(0.2)</td>
<td>0.0(0.1)</td>
</tr>
<tr>
<td>layer-1b</td>
<td>48(4)</td>
<td>0.0(0.2)</td>
<td>0.0(0.1)</td>
</tr>
<tr>
<td>layer-2a</td>
<td>49(4)</td>
<td>0.0(0.1)</td>
<td>0.0(0.1)</td>
</tr>
<tr>
<td>layer-2b</td>
<td>49(4)</td>
<td>0.0(0.1)</td>
<td>0.0(0.1)</td>
</tr>
</tbody>
</table>

Table 6.2: Positions of surface layers, determined from least squares fitting of reflectivity data. Si height parameters are displacements from DAS positions. Pb height parameters are relative to Si layer-1a. The number of atoms are for a 49 atom 7x7 unit cell. The vertical DW-factor (σz) are Gaussian.

The Pb/Si(111)7x7 reflectivity model fit shows that the Pb wetting layer height was determined to be ∼2.6±0.1Å, above the Si-1a layer. The wetting layer density was determined to be ∼0.9±0.1ML. Reducing the density of the Pb-wetting layer increases the oscillatory behavior of the model, because of the interference between Pb ans Si layers, which subsequently reduces the quality of fit. Shifting the Pb-wetting layer height modifies the shape of the cusp below the Si(111)-bragg point near L=2.8: reducing the height produces a sharp
cusp, whereas increasing the height produces a smaller cusp. Consequently, the height and
density for the wetting layer determined by reflectivity is quite sensitive to the wetting layer
height and density.

The model fit shows little sensitivity to the six atom Pb-adatom layer or Si-adatom
layer on the Pb/Si(111)7x7 surface. The model includes the Pb-adatom layer along with
the wetting layer. The Pb-adatom layer was initially chosen to have a height of ∼2.1Å above
Si layer-1a, which was confirmed by rod scattering described below. Removing either the
Si-adatom or Pb-adatom layers do not significantly change the model fit to the data. The
insensitivity results from the low density of both layers as well as the dominance of the
wetting layer in the scattering data. Therefore, reflectivity does not definitively confirm the
existence of the Pb-adatom layer.

The Si layer-1a and layer-1b heights and densities for the Pb/Si(111)7x7 data are un-
modified from the clean Si(111)7x7 mentioned above. Previous studies have assumed that
layer-1a and layer-1b underneath the wetting layer have remained unmodified by the Pb
atoms. Model fit to the Pb/Si(111)7x7 reflectivity data show that the Si layers maintain
their clean Si(111)7x7 positions, and sensitivity to layer heights, ±0.2Å, remains the same
as for the clean Si(111)7x7 fits. Importantly, the wetting layer height above layer-1a must
be maintained to fit the cusp near L=2.8. Consequently, vertically shifting layer-1a, rela-
tive to its clean Si(111)7x7 position, creates oscillations in the intensity at higher L-values,
because the wetting layer must also shift with the layer. Therefore, the presence of Pb does
not significantly modify the height or density of the Si layers.
6.7.2 Stable Wetting Layer Patterson Analysis

Figure 6.17: This figure shows the diffraction data and Patterson map for the stable wetting layer. The map was calculated using Eqn. 3.12, and only positive contours are shown. The map shows the same 8x8 pattern observed previously in Fig. 6.1 [8, 9]. However, the map shows an increased correlation near the center of the half unit cell. This suggests that the density correlation increases with increasing atom distance. The unit cell repeats with the pseudo-symmetric sub-unit cells, drawn in the faulted half of the unit cell.

The Patterson analysis of the Pb/Si(111)7x7 wetting layer follows the pseudo-symmetry of the 7x7 unit cell. In-plane diffraction data was obtained for the stable Pb/Si(111)7x7 surface, as is shown in Fig. 6.1. Comparing previous diffraction data in the literature [8, 9], as shown in Fig. 6.1, the stable wetting layer data shows a much stronger (5\textfrac{2}{7}, 0), relative to other diffraction peaks. The map also shows the 8x8 follows the pseudo-symmetry periodicity of the 7x7. The pseudo-symmetry means that the wetting layer model can be simplified to the pseudo-symmetric sub-unit cell structure factor.

Interestingly, the Patterson Map of the stable wetting layer diffraction data shows a different correlation than previous Patterson analysis, as seen in Fig. 6.1. Figure 6.17 shows the Patterson Map of the stable wetting layer. The correlation decreases with increasing bond length, as was shown in the literature. However, the correlation increases toward the
center of the pseudo-symmetric unit cell, which was not previously observed. The corner positions are self correlations and defined as unity. The nearest-neighbor 8x8 bond distance has a correlation of 0.8. The second and third 8x8 correlation distances drop to ~0.6. The center of the half unit cell has three atoms with correlation of 0.7. The increased correlation suggests increased 8x8 ordering for bond lengths on the order of the pseudo-symmetric unit cell distance.

6.7.3 Pb/Si(111)7x7 Wetting Layer Model

This section presents the structure factor calculations used to model the experimental scattering data of the Pb/Si(111)7x7. The basic 8x8 structure factor determined from Patterson mapping, in sec. 6.1, is used as the basis for the model. Consequently, the model represents only the wetting layer structure factor, and must be added to the Si(111)7x7 structure factors to fit the scattered data. Importantly, the model utilizes the pseudo-symmetry operations outlined in sec. 4.3. Consequently, it is useful to use the pseudo-symmetric unit cell outlined in the 8x8 Patterson map in fig. 6.17. The origin of the model presented here is the same as the Si(111)7x7 unit cell indicated in fig. 2.8.
Figure 6.18: This figure shows the vertical positions of the Pb/Si(111)7x7 model, and the vertical fitting parameters. The Si layers are indicated as red rectangles, and the Pb layers are blue. The Solid arrows indicate the position of Si layers in the bulk Si(111) model, relative to layer-3a. Consequently, the vertical layer parameters \((z_{2b}, z_{2a}, z_{1b}, z_{1a})\) represent deviations from bulk Si(111) positions. However, the top three layer (Si adatom, Pb-adatom, and wetting layer) height parameters are referenced to the total layer-1a height \((c \frac{7}{12} + z_{1a})\). Finally, the Pb atoms within the wetting layer have a height parameter \((z_j)\) relative to the total wetting layer height\((c \frac{7}{12} + z_{1a} + z_{wetting})\).
Figure 6.19: This figure shows the in-plane positions of the Pb/Si(111)7x7 model, and atom index for the fitting parameters. (a) The commensurate 8x8 lattice in the 7x7 unit cell has 64 Pb atoms per unit cell. (b) Utilizing the pseudo-symmetry of the 7x7 unit cell simplifies the model to 10 Pb atoms. The index for each atom is used for the fitting parameters in eqn. 6.4. The direction of in-plane strain is indicated for each atom. Atoms (1,5) are not allowed to displace in-plane.

The structure factor calculations are based on the vertical and in-plane positions given in Figures 6.18-6.19. The wetting layer has an average height parameter ($z_{\text{wetting}}$) referenced to layer-1a. Consequently, the wetting layer shifts with layer-1a height parameter ($z_{1a}$). Also, each atom has a height parameter ($z_j$) relative to the average wetting layer height. Having two separate wetting layer parameters leads to a possible degeneracy, when fitting data. To limit degeneracy, the average wetting layer parameter was determined from fitting
reflectivity data. Subsequently, the average layer parameter was held fixed when fitting in-plane diffraction and rod scattering, and only the relative height parameters were allowed to change. The in-plane positions of the wetting layer model were based on the pseudo-symmetric 8x8 unit cell. The wetting layer has the same in-plane origin as layer-1b in Fig. 2.8. Pb atoms initially occupied ideal 8x8 lattice sites. Displacement from 8x8 was directed toward the origin of the unit cell, except for atoms 1, 5, and 10. Importantly, atoms along pseudo-symmetry lines are only allowed to displace parallel to the mirror planes. Finally, the combined vertical and in-plane motions of the Wetting layer were put into the structure
factor calculation:

\[
F_{\text{total}}(H, K, L) = F_{S(111)}(H, K, L)e^{2\pi i \frac{(2H+K)}{2}} \quad \text{(equation 4.1)}
\]

\[
+ F_{2b}(H, K, L, z_{2b}, \Delta_{2b}) \quad \text{(equation 4.1)}
\]

\[
+ F_{2a}(H, K, L, z_{2a}, \Delta_{2a}) \quad \text{(equation 4.1)}
\]

\[
+ F_{7;7'}(H, K, L) \ast e^{iQz_7 \lambda} \quad \text{(equation 4.1)}
\]

\[
+ F_{\text{wetting}}(H, K, L) \ast e^{iQz_8 \lambda} \ast e^{-\frac{i}{2}Qz_{8}^{2}\lambda_{\text{wet}}} \ast e^{-\frac{i}{2}Qz_{8}^{2}\lambda_{\text{wet}}}
\]

where \( \rho_j \) is the atom density, and \( \zeta_j \) is the atom displacement from 8x8. The double counting which occurs for pseudo-symmetry operations, mentioned in 4.3, is explicitly corrected in the model. Consequently, the occupancy parameters for each atom are relative to complete occupancy on the surface, and do not correct for the double counting. Also, \( Q_{//} = 2\pi \sqrt{\frac{4(H^2+HK+K^2)}{a^2}} \) is the in-plane reciprocal space momentum transfer.
6.7.4 Two-Dimensional Diffraction and Structural Model

Figure 6.20: This figure shows the in-plane 2D-diffraction map of in-plane 7x7 structure factors taken at \( L = 0.1 \). The area of each half circle is proportional to the structure factor, with the experimental data on the left and model fit on the right. The integer-Si positions are shown as p6mm hexagons. The mirror symmetry lines are indicated by dotted line, while the symmetry line creating the faulted/unfaulted mirror symmetry is indicated by the solid line.

Figure 6.20 shows the in-plane \((\frac{7}{7}, \frac{4}{7}, 0.1)_{H}\) diffraction data of the stable Pb/Si(111)7x7 wetting layer, with experimental data as the left half-circle and model fit as the right half-circle. In-plane, 176 diffraction peaks were measured in the experiment. The 176 peaks were averaged across the \((h=k)\) six-fold (p6mm) mirror symmetry line, resulting in 96 symmetry-unique diffraction peaks. Consequently, the diffraction figure shows 192 peaks, resulting from the 96 plotted on both sides of six-fold the mirror-plane. The structure factor for each peak is proportional to the area of each half circle. The symmetry unique data set is given in appendix C, for raw and geometry corrected data.
It is useful to have a quantitative measure of the validity for assuming six-fold-symmetry of the wetting layer. For example, a previous study of Au/Si(111)7x7 showed that Au atoms only occupy the faulted half of the unit cell and violate six-fold symmetry [33]. The degree to which the Pb wetting layer follows six-fold symmetry was estimated from the total standard deviation ($\varepsilon$) of the in-plane diffraction data, which was obtained by symmetry averaging the data. The standard deviation includes both systematic errors as well as possible deviations from six-fold symmetry. Consequently, the measurement of six-fold symmetry is as good as the systematic error if not better. The standard deviation was calculated for both clean Si(111)7x7 and the Pb/Si(111)7x7 surfaces. The calculation used the same peaks for both surfaces, which were limited to 20 peaks and their symmetry equivalent positions. The total standard deviation for the Pb/Si(111)7x7 yielded $\varepsilon=0.042$, while the clean Si(111)7x7 surface resulted in $\varepsilon=0.084$. The small standard deviation for the Pb/Si(111)7x7, as well as the reduction in error compared to the clean surface, indicates the wetting layer follows the six-fold symmetry of the 7x7 unit cell.

The qualitative behavior of diffraction peak intensities also indicate a strained 8x8 ordering within the wetting layer. The ($\frac{8}{7}, 0)_H$ is the dominant peak on the diffraction pattern, which would support the 8x8 model previously proposed [8, 9]. However, the diffraction data also indicates strain in the wetting layer, because other 7x7 peaks also show intensity. For example, the ($\frac{1}{7}, 1)_H$ structure factor is half, and the ($\frac{2}{7}, 0)_H$ structure factor is one third of the ($\frac{8}{7}, 0)_H$ structure factor. In fact, a general pattern of the diffraction data shows the structure factor for the 7x7 peaks decreases with increasing distance from the ($\frac{8}{7}, 0)_H$. The collection of diffraction peaks near the ($\frac{8}{7}, 0)_H$ represents a first order diffraction pattern, and the collection near the ($\frac{16}{7}, 0)_H$ is a second order set. However, unlike the first order pattern which is dominated by a single strong ($\frac{8}{7}, 0)_H$ intensity, the second order pattern
has $(\frac{15}{7}, 0)_H$ structure factor is equivalent to the $(\frac{16}{7}, 0)_H$ structure factor. An ideal 8x8 layer would only have strong multiples of $(\frac{8}{7}, \frac{8}{7})_H$ and no others. Therefore, the first and second order diffraction peaks indicated the wetting layer does not follow a perfect 8x8.

**Layers of Atoms**

Figure 6.21: This figure shows the real-space model describing the surface structure for Pb/Si(111)7x7 interface. The initial Si layer-1a and layer-1b are as described previously, without the Si-adatom layer. The pseudo-symmetric sub-unit is shown on the faulted unit cell half. The unit cell origin is the lower left corner, for each layer. The Si-6x6 layer sits 1.0Å above the Si layer-1a, with 3 Si atoms along the edges of the sub-unit cell. The Pb-adatom layer sits 2.1Å above the Si layer-1a, and has six Pb-atoms per unit cell. Finally, the strained Pb-8x8 layer sits 2.6Å above the layer-1a. Ideal 8x8 sites are represented by circles with single dashed lines. Atoms near the unit cell corners, represented by circles having double solid lines, are shifted toward the corner sites. The remaining atoms shift toward layer-1a sites as indicated by arrows.
Figure 6.21 shows the wetting layer model, which reproduces the diffraction data. The figure shows the pseudo-symmetric sub-unit cell for each layer in the model. The pseudo-symmetry operations of the sub-unit cell reproduce the entire 7x7 unit cell [15]. The model was forced to follow the symmetry operations of the pseudo-symmetric sub-unit cell, because the pseudo-symmetry restriction simplifies the structural analysis and reduces the number of model parameters, as outlined in section 2.3.1. This restriction is supported by the standard deviation of symmetry analysis done above, and by the symmetry observed in the rod data described below. Each layer is given in a separate panel in 6.21, with heights relative to Si layer-1a. Importantly, the diffraction data is dominated by the Pb wetting layer in the model, just as specular reflectivity. Therefore, the wetting layer in fig. 6.21(d) dominates the model fit to the diffraction data.

The densely packed Pb wetting layer, shown in fig. 6.21(d), exhibits the distributed Pb atom strain indicated in the diffraction pattern. Initially, all Pb atoms were set to occupy the ideal 8x8 lattice sites, as outlined in section 6.7.3. Subsequently, Pb atom positions and occupancy were varied with least-squares refinement. As can be seen, atoms Pb-(8,10) maintain their ideal 8x8 positions, whereas atoms Pb-(2,4,6,7) shift toward the unit cell corner. Pb-(2,6) atoms lead to the strong structure factor observed in the $(\frac{1}{2}, 1)_{H}$ peak because of their off-symmetry bond direction. Interestingly, atoms labeled Pb-(1,3,5) were found to have no occupancy because their positions would create intensity not observed in the diffraction data. Pb-9 was found to be completely occupied. However, its vertical position is indistinguishable from Pb-11 (Pb-adatom) with in-plane diffraction. This distinction will be clarified with rod scattering below.

It is useful to quantitatively compare our model with previous models of the wetting layer. We used $\chi^2$-analysis with our current in-plane diffraction data set in fig. 6.21 to
compare models. The Pb-8x8 model gives a $\chi^2=12$, while the Pb-1a model gives a $\chi^2=64$ which is considerably worse. Our strained wetting layer model gives a $\chi^2=3$, which is significantly better than both previously proposed models considered here. However, $\chi^2$-analysis of in-plane diffraction does not give a complete representation for comparing the three-dimensional structural models. As presented below, fractional rod scattering provide further constraints which have important qualitative implications.

6.7.5 Rod Scattering

Fractional rod scattering provides important constraints on the vertical heights for atomic positions, as well as provide additional constraints on the in-plane structure. Furthermore, the fractional rod constraints help to eliminate degenerate models of the data. The strength of the rod scattering is related to the amount of Pb in different layers of the surface. Figure 6.22 shows the structure factor ($|F|$) for the fractional rods of the first order in-plane diffraction peaks $(\frac{8}{7}, 0)_H, (\frac{9}{7}, 0)_H, (\frac{1}{7}, 1)_H$, with two of their p6mm symmetry equivalent rods. The first order rods are the strongest fractional rods, and provide evidence of wetting layer atom positions on the surface; whereas, the fractional rods for the second order diffraction peaks $(\frac{13}{7}, 0)_H, (\frac{15}{7}, 0)_H$, and $(\frac{16}{7}, 0)_H$ in fig. 6.23 are more sensitive to the Pb-adatom layer and Si-dimer atoms in layer-1b. Interestingly, the first order $(\frac{6}{7}, 0)_H$ fractional rod, in fig. 6.24, provides evidence of Si adatom displacement on the surface, which has not previously been observed. Finally, the bulk Si(111) rods (1,0),(0,1),(1,-1),(1,1), and (2,0) provided information on atomic registration with the bulk substrate which may be missed in fractional rods.

The two main features of rod scattering are the periodicity and the amplitude of the structure factor. Because there are a limited number of surface layers, there is no Bragg
scattering observed along a fractional rod. However, there is still an interface between the surface layers, which does change the scattering. For example, if there were only two perfect Pb 8x8 layers with a vertical distance of $d=3\,\text{Å}$ on the surface, then the $(\frac{8}{7},0)_H$ rod scattering would have an oscillating intensity with a periodicity of $\Delta L \sim \frac{c}{d} = 3.3\text{rlu}$. Furthermore, the amplitude of the rod oscillations for each period would be uniform with $L$, such that the intensity of the rod would be the same at $L=0,3,6$ for the rod. Therefore, rod data provides evidence for the density and relative heights for just the surface layers that are commensurate with the 7x7.
Figure 6.22: This figure shows the first order fractional diffraction rods \((0,8/7)(1/7,1)(9/7,0)\) and their p6mm equivalent rods normalized to the \((8/7,0,.1)\) structure factor. The strained wetting layer model fit (solid lines), given in fig. 6.21, as well as a previously proposed Pb-1a model (Dashed lines) [10]. The wetting layer model fit compares well with the overall smoothly varying data. In contrast, the Pb-1a model does not get the overall scale correct for the \((1/7,1)\) and \((9/7,0)\) rods. Also, the Pb-1a model over-reports the amplitude of oscillation for the rods. However, the rods are not sensitive to the low density Pb-adatom layer. Removing the Pb-adatom layer (dashed line) does not change the \((8/7,0,L)\) rod, and has limited impact on the \((1/7,1,L)\) or \((9/7,0,L)\) rods.

Fractional rod scattering also provides stronger evidence that the Pb/Si(111)7x7 surface follows six-fold symmetry than in-plane diffraction, because of the extra out-of-plane scattering constraint. In-plane diffraction provides sensitivity to major six-fold symmetry violations, such as Pb atoms only occupying the faulted half of the unit cell. However, fractional rod scattering is more sensitive to smaller symmetry violations. For example, if
the wetting layer included some missing Pb atoms in the unfaulted half of the unit cell, then the mirror symmetry would only be slightly broken. Consequently, the \((\frac{8}{7}, 0, L)_{H}\) rod would have a more damped amplitude of oscillation than the \((0, \frac{8}{7}, L)_{H}\) rod, because there would be more Pb atoms interacting with the Si substrate in the \((\frac{8}{7}, 0, L)_{H}\) rod. Furthermore, if Pb atoms on the faulted half of the unit cell had a uniformly different height than Pb atoms on the unfaulted half of the unit cell, then the periodicity would be different between the symmetry equivalent rods. The data for the first order rods clearly show that there is no deviation from six-fold symmetry, either in amplitude oscillation or periodicity. Therefore, the wetting layer does not have any atoms which deviate from the six-fold symmetry in either occupancy or height.

The first order rod data confirm the reflectivity measurement that the majority of Pb atoms occupy the wetting layer at a vertical height of \(\sim 2.65\text{Å}\) above layer-1a. Qualitatively, the period of oscillation in the first order rods \((\Delta L=3.5)\) corresponds with a layer height of \(d\sim \frac{c}{5.5}=2.65\text{Å}\). It is important to note that fractional rod data only provide layer heights relative to other surface layers. Consequently, the periodicity for the first order rods could correspond to interference between the wetting layer and Si layer-1a or layer-1b; whereas, reflectivity data provide vertical layer positions relative to all of the Si layers, including the bulk Si(111) substrate. Therefore, correlating the observation from fractional rod oscillations with reflectivity shows that the interference observed in first order rod data involves the wetting layer and Si layer-1a.
Figure 6.23: This figure shows the structure factors for the second order fractional rods (13/7,0), (15/7,0), and (16/7,0). The structure factor data have all been normalized to the (8/7,0,.1) structure factor. The strained wetting layer model fits, shown in Fig. 6.21, (solid lines) accurately reproduces the behavior of each rod. The model fit without the Pb-adatom layer (dashed line) is shown with the (13/7,0) and (15/7,0) rod data. Finally, the model fit with the Pb-adatom layer at 2.0Å(dotted-dashed line), above layer-1a, is shown with the (13/7,0) rod data.

The periodicity of the first order rod data also show that layer-1b Si-atoms do not significantly contribute to the rod scattering. Because layer-1b follows the bulk Si(111) stacking symmetry, the layer does not contribute to fractional rod scattering unless atoms within the layer deviate from their T1-sites. If the layer-1b atoms did significantly deviate from their positions, then the periodicity of the rod oscillations would not correspond to 2.65Å. Therefore, first order rod scattering eliminates any model which significantly modifies the
layer-1b Si-atoms.

The amplitude of the first order fractional rod oscillations also confirm that the Pb/Si(111)7x7 surface consists of a dense wetting layer above the Si 7x7 layers. If the rod scattering resulted from two equally dense layers, then the amplitude of oscillation along the rod would be equal, as discussed previously. However, if the scattering corresponded with a higher density top layer, then the rod data would be smoothly decaying with weaker amplitudes. Thus, the first order oscillation show that the wetting layer dominates the rod scattering. This is further supported when comparing the previously proposed Pb-1a model to the first order fractional rod data. The Pb-1a model fit to the $(\frac{3}{7}, 0)_H$ and $(\frac{1}{7}, 1)_H$ rods show that the model predicts the Pb wetting layer and Si layers result in stronger amplitudes of oscillation than the data shows. Also, the model predicts a larger scale factor at the $(\frac{1}{7}, 1)_H$ than the data shows. Thus, the Pb-1a model comparison to rod data show that Pb atoms do not sit above Si sites, and that Pb atoms contribute significantly more scattering power to the rod data than the Si layers.
Figure 6.24: This figure shows the Pb/Si(111)7x7 (6/7,0) and p6mm equivalent rods along with the clean Si(111)7x7 rod, normalized to the (8/7,0,.1) structure factor. The clean Si rod shows a smoothly varying structure factor, which is fit (solid line) with the previously determined Si atom positions, from reflectivity. In contrast, the Pb/Si(111)7x7 rods show a sharp cusp at L=0.1 with maximum amplitude around L=0.3. The model fit (solid line) captures this feature with the Si-6x6 layer shown in Fig. 6.21. The best fit without the Si-6x6 layer (dashed line) cannot reproduce the position of the cusp or the relative structure factor heights at the peaks. Shifting the Pb-adatom height (dotted dashed line) shifts the cusp to higher L-values.

An interesting observation of the first order (6/7, 0, L) rod shows that there is a strong interference which is not observed in any other rod. It is quite dramatic when compared to the (6/7, 0, L) rod data on the clean Si(111)7x7, as seen in fig. 6.24. The Si(111)7x7 surface shows a smoothly varying rod modeled with the ideal Si(111)7x7 atomic positions. In contrast, the presence of Pb on the Si(111)7x7 surface drastically changes the behavior of the rod, although the structure factor scale of the rod remains low indicating the scattering density involved is low. The Pb/Si(111)7x7 data shows a sharp cusp at L=1.0 in the rod,
and a maximum amplitude at $L=3.0$ rlu which is greater than the amplitude at $L=0$ rlu.

The cusp position and amplitude ratios are the same for the symmetry equivalent $(0, \frac{6}{7}, L)_H$ and $(-\frac{6}{7}, \frac{6}{7}, L)_H$ rods, which indicate the atomic structure is six-fold symmetric, as with the first order rods. However, unlike the smoothly varying first order rods, the sharp cusp of the $(\frac{6}{7}, 0, L)_H$ rod is more sensitive to small variations of the unit cell, because the cusp is caused by a greater interference between atoms on the surface. Furthermore, the low intensity of the rod suggests that the interference does not result from wetting layer motion.

We propose that the model in Fig. 6.21(b) explains the observations of the $(\frac{6}{7}, 0, L)_H$ rod. First, the fit using the initial clean Si(111)7x7 and wetting layer positions, in fig. 6.21(d), does not capture the position of the cusp or the relative amplitude of oscillations in the rod data. Furthermore, no atomic displacement within the wetting layer could reproduce the observed $(\frac{6}{7}, 0, L)_H$ rod. Instead, an initial model fit to the rod involves a 6x6 lattice of Si atoms expanded to be commensurate with the 7x7 unit cell. The resulting 6x6 lattice fit results in a site occupancy of $\sim 0.33$ for all 36 sites, and height of 1.0Å. Importantly, the overall density of the 6x6 layer corresponds with the same number of Si adatoms ($0.33*36 \sim 12$ Si atoms). The occupancy and height of the model fit indicate that the rod can be explained by displacing the Si(111)7x7 adatoms on the surface. However, some of the 6x6 lattice sites would result in non-physical Pb-Si bond lengths. Therefore, we propose that the majority of atoms transition toward the 6x6 sites at the edge of the unit cell.

This adatom displacement can be compared with previous STM observations. Coverage-dependent STM analysis proposed that Si adatoms move from their Si(111)7x7 positions in the presence of Pb atoms [19, 20, 10]. The Si displacement was observed for Pb coverage above 0.12ML. However, in those models the Si adatoms randomly occupied other sites on the surface, intermixing with the deposited Pb-atoms. The coverage-dependent STM
observations suggest that an important test of the Si-adlayer model would be to scan the $(\frac{6}{7}, 0, L)_H$ rod as a function of Pb coverage.

Figure 6.25: This figure shows the structure factor $|F|$ of $(1,0)(0,1)(1,-1)$ bulk rods on the left panel, and $(1,1)(2,0)$ bulk-Si(111) rods on the right panel. The Pb 8x8 model (dashed line) gives the same fit profile as a clean Si(111)7x7, because few 8x8 sites are coincident with the bulk Si(111) 1x1 lattice sites. The model, from fig. 6.21, (solid line) fits well to the observed. Removing the Pb-11 atoms (dotted-dashed line) from the model reduces the quality of fit on the $(1,1)$ and $(2,0)$ rods, but does not significantly affect the $(1,0)$, $(1,-1)$, or $(0,1)$ rod profiles.

Fractional and bulk rod data provide evidence for the Pb-adatom layer, shown in fig. 6.21(c). Importantly, the Pb-11 sites in the Pb-adatom layer are coincident with the Pb-9 sites in the wetting layer, although they are at different vertical heights. Although the sites cannot be distinguished by 2D diffraction, their vertical positions can be determined by rod scattering, thus distinguishing the sites. The strongest evidence for the existence of the Pb-11 layer height comes from the $(\frac{6}{7}, 0)_H$, $(\frac{13}{7}, 0)_H$, and $(2, 0)_H$ rods. The initial evidence comes from the periodicity of the $(\frac{13}{7}, 0, L)_H$ rod. The period corresponds with a lattice spacing of $\sim 3.8 \pm 0.1\text{Å}$. The period is close to the distance between Pb-11 and the Pb-(7,10)
atoms in the wetting layer. Thus, the periodicity suggests that the Pb-adatom layer has a height of 2.0 Å above Si layer-1a, which was the initial height chosen for the model.

The constraints from all three fractional rods provided the final model height of the Pb-adatom layer, which was determined to be 2.1 ± 0.1 Å above layer-1a using least-squares fitting. By removing the Pb-adatom layer from the model fits, the structure factor of the \((\frac{13}{7}, 0, L)_H\) rod decreases, and the cusp of the \((2, 0)_H\) at \(L=0.5\) becomes dampened. The reduced quality of fit for the two rods show the importance of including the layer in the model. The layer height has two competing constraints indicated from the model fits: the location of the sharp cusp in the \((2, 0, L)_H\) rod at \(L=0.5\), as well as the cusp in the \((\frac{6}{7}, 0, L)_H\) rod suggest that the Pb-adatom height is 2.2 Å above layer-1a, whereas the periodicity of the \((\frac{13}{7}, 0, L)_H\) suggests a height of 2.0 Å above Si layer-1a. These two mutually exclusive constraints provided the limits of the accuracy for the vertical layer position in the model.
Table 6.3: Atomic positions of Pb/Si-atoms at the Pb/Si(111)7x7 surface, obtained from least-squares refinement to the data. The positions are given in Cartesian coordinates: the x-axis is aligned with $\vec{a}_1^*$ and the y-axis is perpendicular, as seen in Fig. 6.21. The origin of the coordinates is the hexagon at the pseudo-symmetric unit cell corner. The height if the wetting layer Pb atoms is the addition of vertical parameters ($z = z_{wet} + z_j$) as shown in Fig. 6.18.

<table>
<thead>
<tr>
<th>Atom index</th>
<th>x (Å)</th>
<th>y (Å)</th>
<th>z (Å)</th>
<th>Occupancy</th>
<th>$\sigma_r$ (Å)</th>
<th>$\sigma_v$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-wetting layer</td>
<td></td>
<td>z=Height above Si layer-1a</td>
<td></td>
<td></td>
<td>0.35(0.1)</td>
<td>0.2 (0.1)</td>
</tr>
<tr>
<td>Pb-1</td>
<td>0(0.0001)</td>
<td>0(0.0001)</td>
<td>0(0.2)</td>
<td>0(0.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-2</td>
<td>2.62(0.04)</td>
<td>0(0.034)</td>
<td>3.03(0.2)</td>
<td>0.75(0.25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-3</td>
<td>6.72</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0(0.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-4</td>
<td>10.08(0.02)</td>
<td>0(0.017)</td>
<td>2.55(0.2)</td>
<td>0.7(0.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-5</td>
<td>13.44</td>
<td>0.0</td>
<td>2.7</td>
<td>0.0(0.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-6</td>
<td>4.18(0.04)</td>
<td>2.4(0.04)</td>
<td>2.7(0.2)</td>
<td>0.8(0.15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-7</td>
<td>8.12(0.015)</td>
<td>2.81(0.013)</td>
<td>2.7(0.2)</td>
<td>1.0(0.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-8</td>
<td>11.76(0.01)</td>
<td>2.91(0.009)</td>
<td>2.7(0.2)</td>
<td>1.0(0.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-9</td>
<td>9.3</td>
<td>5.33</td>
<td>2.7</td>
<td>0.0(0.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-10</td>
<td>13.44(0.001)</td>
<td>5.82(0.001)</td>
<td>2.7(0.2)</td>
<td>1.0(0.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb-adatom layer</td>
<td></td>
<td>z=Height above Si layer-1a</td>
<td></td>
<td></td>
<td>0.4(0.2)</td>
<td>0.2(0.1)</td>
</tr>
<tr>
<td>Pb-11</td>
<td>10.08(0.001)</td>
<td>5.8(0.001)</td>
<td>2.1(0.3)</td>
<td>1.0(0.2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si Adatom layer</td>
<td></td>
<td>z=Height above Si layer-1a</td>
<td></td>
<td></td>
<td>0.2(0.2)</td>
<td>0.0(0.1)</td>
</tr>
<tr>
<td>Si-1</td>
<td>4.38(0.01)</td>
<td>0.0</td>
<td>1.0(0.4)</td>
<td>0.9(0.15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-2</td>
<td>8.77(0.01)</td>
<td>0.0</td>
<td>1.0(0.4)</td>
<td>0.9(0.15)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-3</td>
<td>13.16(0.01)</td>
<td>0.0</td>
<td>1.0(0.4)</td>
<td>0.9(0.15)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The atomic positions and occupancies that we have determined for the model are given in table 6.3, with the atom index from Fig6.21. The nearest-neighbor bond lengths are given in table 6.4. Atoms near the unit cell corners take bond lengths close to Pb-Pb ionic bond (2.6 Å). Whereas, atoms near the center of the unit cell take bond lengths that are closer to ideal 8x8 lengths (3.36 Å) and metallic Pb-Pb bond lengths (3.6 Å). The resulting atomic positions from model fits to the data show that Pb-atoms in the wetting layer cluster around the corners and centers of the unit cell.

The total occupancy for all Pb atoms equals in the model gives a wetting layer coverage from 0.5ML to 0.825ML. The variation in coverage results from the large number of available parameters in the model. The coverage determined from best least-squares fit to the

<table>
<thead>
<tr>
<th>nearest neighbors</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb2-Pb6</td>
<td>2.9(0.2)</td>
</tr>
<tr>
<td>Pb2-Pb4</td>
<td>7.4(0.2)</td>
</tr>
<tr>
<td>Pb2-Pb2’</td>
<td>2.6(0.15)</td>
</tr>
<tr>
<td>Pb2-Si1</td>
<td>2.7(0.3)</td>
</tr>
<tr>
<td>Pb4-Pb7</td>
<td>3.6(0.25)</td>
</tr>
<tr>
<td>Pb4-Pb8</td>
<td>4.2(0.01)</td>
</tr>
<tr>
<td>Pb4-Si1</td>
<td>5.9(0.2)</td>
</tr>
<tr>
<td>Pb4-Si2</td>
<td>2.1(0.3)</td>
</tr>
<tr>
<td>Pb6-Pb7</td>
<td>3.9(0.4)</td>
</tr>
<tr>
<td>Pb7-Pb7’</td>
<td>3.25(0.05)</td>
</tr>
<tr>
<td>Pb7-Pb8</td>
<td>3.6(0.2)</td>
</tr>
<tr>
<td>Pb7-Pb11</td>
<td>3.6(0.2)</td>
</tr>
<tr>
<td>Pb8-Pb10</td>
<td>3.36(0.2)</td>
</tr>
<tr>
<td>Pb10-Pb11</td>
<td>3.4(0.2)</td>
</tr>
<tr>
<td>Pb11-Si</td>
<td>2.2(0.3)</td>
</tr>
</tbody>
</table>

Table 6.4: Bond lengths for Pb/Si-atoms at the Pb/Si(111)7x7 interface. This table is obtained by calculating the atomic position differences given in table 6.3. The primed index indicate nearest-neighbor pseudo-symmetry atoms.
data is \( \sim 0.75\text{ML} \), and is consistent with wetting layer density determined from reflectivity. Reducing or increasing the coverage lowers the quality of fit to the data. Also, STM studies have suggested that the coverage of the wetting layer is \( \sim 0.85\text{ML} \) [10].

The discrepancy in Pb coverage likely results from Pb atoms occupying alternative structures on the surface. Above \( \sim 30^\circ C \) bulk Pb crystals begin to form on the surface, and consume the wetting layer [3, 2]. Also, STM analysis shows that defect wetting layer structures can form on the surface, depending on sample preparation [10]. Both the Pb-crystals and defect wetting layer structures would not contribute the 7x7 diffraction spots. Therefore, the stable wetting layer model based solely on the 7x7 diffraction pattern would not account for all Pb atoms on the surface.

### 6.8 Conclusions

In this thesis we have studied the Pb/Si(111)7x7 wetting layer. We found that the wetting layer structure can change over a broad temperature range. When grown at low temperature \( (30^\circ C < T < 150^\circ C) \) the wetting layer increased its order toward a better ordered 8x8. When grown at higher temperature \( (>150^\circ C) \) the entire Pb/Si(111)7x7 transitioned to a Pb/Si(111)1x1. Understanding these kinetic issues were necessary in order to produce and study a stable Pb/Si(111)7x7 wetting layer structure.

We solved the structure for the stable Pb/Si(111)7x7 surface using X-ray scattering. We used reflectivity, in-plane diffraction, and rod scattering to determine the three-dimensional positions of Pb and Si atoms at the surface. The wetting layer involves a large unit cell of 64 Pb and 102 Si sites. The commensurate strained structure shows that Pb atoms in the wetting layer are distributed between 8x8 sites and nearby layer-1a sites. Also, Pb atoms
cluster near the corner and center of the 7x7 unit cell.

The structural model combined with kinetic observations also account for the different structural models that have been proposed in the literature [8, 9, 20, 10]. We showed that the wetting layer grown <150°C increases its order toward 8x8. STM analysis, by other, showed that Pb atoms initially occupy sites directly above Si 7x7 atoms [19]. It is likely that the low temperature kinetic behavior we observe involves the transition of Pb atoms from their initial sites above Si atoms toward their preferred strained 8x8 sites. This transition would explain the strained structure that we have observed in our near-equilibrium surface as well as the discrepancy between previous structural models in the literature.

In summary, this thesis solves a long-standing problem. Reports in the literature have proposed different crystalline structures and some have claimed that it is amorphous. One of our key discoveries was that the wetting layer is out of equilibrium over a surprisingly broad temperature range of ~150°C. Once we understood this, we could produce a wetting layer that was in quasi-equilibrium and solve its structure. Our structural analysis went beyond using conventional in-plane diffraction. Instead, we also employed crystal truncation rods that additionally constrained the model as well as determine vertical structure. Although, our studies have not directly determined the origin of the fast kinetics of the QSE nano-crystals that is thought to be enabled by the wetting layer. The ease to which Pb atoms can move in the wetting layer over a broad temperature range might turn out to be an important piece of the puzzle. Finally, it is hoped that the determination of the structured parameters as well as mobility activation barriers might provide new insight into the fast kinetics in this QSE system.
Appendix A

Patterson/Fourier Difference Mapping

This appendix provides the c-code used for creating Patterson and Fourier Difference maps used in this thesis. The code provides an important description on how to computationally create Fourier maps using diffraction data.
/* BY : MICHAEL GRAMLICH */

/* This Program will create a Fourier Difference Map */
/* of the Integrated Intensity peaks from a Theoretical */
Pb/Si(111) data set */

/* *************************************************************/
/* NOTES: READ BEFORE OPERATING THIS PROGRAM */
/* */
/* (1) Specify Input Data file in *model within loop */
/* */
/* (2) Specify Output Data file *pfile at declaration */
/* */
/* (3) Specify if HK values read in are integer or */
/* are in fractional (i.e. Sometimes the (1/7,0) */
/* is actual given as a (1 0) in the file */
/* */
/* (4) The number of columns in the data file must */
/* manually be coded in the fscanf(). Change this */
/* function accordingly. */
/* */
/* *************************************************************/

#include <stdio.h>
#include <math.h>
#include <complex.h>

#define PI 3.14159

int difference_function_2D(int columns, char *output_file, char *input_file, int scale)
{
    FILE *model;
FILE *pfile = fopen(output_file,"w") ; // Pointer storage for data

float h,k;
float x,y;
float Area1=0.0, alphahk=0.0, error1=0.0; // Values for data-set
float Area2=0.0, alphahk2=0.0, error2=0.0, blank1; // Values for model

complex Difference=0.0, Difference2=0.0;
float dq, dg;
int mol;

for (x=0.0;x<7.0;x+=0.1){for (y=0.0;y<7.0;y+=0.1){
    Difference = 0.0;
    Difference2 = 0.0;
    // Open the Model file for reading
    // model = fopen(input_file,"r");

    while(fscanf(model, "%f\t%f\t%f\t%f\t%f\t%f", &h, &k, &Area1, &alphahk, &Area2, &alphahk2) != EOF)
    {
        // This will ensure you don't use the integer values for inversion//      
        // If h,k values are in fractions (i.e.
        // (1/7,0) is 0.142857 0 in file //
        if(scale == 0){mol = ((int)(h*7.007))%7 + ((int)(k*7.001))%7;}
        // If h,k values are in integers (i.e.
        // (1/7,0) is 1 0 in file //
        if(scale == 1){mol = ((int)h)%7 + ((int)k)%7;}

        if(mol !=0){
            Difference += (sqrt(Area1)-sqrt(Area2))*cexp(-I*(2.0*(double)PI*(((double)h*(double)x)+((double)k*(double)y))-(double)alphahk));
            Difference2 += (sqrt(Area1)-sqrt(Area2))*cexp(-I*(2.0*(double)PI*(((double)h*(double)x)+((double)k*(double)y))-(double)alphahk2));
        }
    }
    dq = creal((float)Difference);
    dg = creal((float)Difference2);
}
int patterson_function_2D(int columns, char *output_file, char *
input_file, int scale)
{
FILE *model;
FILE *pfile = fopen(output_file,"w") ;// Pointer storage for data

float h,k;
float x,y;
float Area1=0.0, alphahk=0.0, error1=0.0; // Values for data-set 1
float Area2=0.0, alphahk2=0.0, error2=0.0, blank1; // Values for model

complex Difference=0.0, Difference2=0.0;
float dq, dg;
int mol;

for (x=0.0;x<7.0;x+=0.1){for (y=0.0;y<7.0;y+=0.1){

    Difference = 0.0;
    Difference2 = 0.0;
    // Open the Model file for reading
}
model = fopen(input_file,"r");

while(fscanf(model, "%f\t%f\t%f\t%f", &h, &k, &Area1, &alphahk) != EOF)
{
    // This will ensure you don't use the integer values for inversion/
    // If h,k values are in fractions (i.e. (1/7,0) is 0.142857 0 in file //
    if(scale == 0){mo1 = ((int)(h*7.007))%7 + ((int)(k*7.001))%7;}
    // If h,k values are in integers (i.e. (1/7,0) is 1 0 in file //
    if(scale == 1){mo1 = ((int)h)%7 + ((int)k)%7;}
    if(mo1 !=0){
        Difference += Area1*cos((2.0*(double)PI*(((double)h*(double)x)+((double)k*(double)y))));
    }
}

dq = creal((float)Difference);

fprintf(pfile,"%f\t%f\t%.1f\n",x,y,dq);
fclose(model);
}

fclose(pfile);
printf("Patterson Map Complete.\n");
Appendix B

Log and Data Files

B.1 Example Log File
B.2 Example Data File
B.3 D-Plot Software For Fit Peak Plotting

This appendix provides an example macro used for plotting in-plane diffraction data using the D-plot plotting software.
This macro will plot 2D-diffraction data as a bubble plot, with proper scales. For both model and experimental data.

Note the data file is formatted as follows:

\[ K-0.04\times\sqrt{\text{Imodel}}, H, \text{Imodel}, K-0.04\times\sqrt{\text{Iexp}}, H, \text{Iexp} \]

The macro will read each data set and put in proper format.

Directory("C:\Research\PhD Thesis\Figures\Clean-Si-inplane")

Filetype(4)
ColumnsAre(0,1,2,3)

FileOpen("test-map.dat")
Bubbles(1,955,2,10,500,0,0,,0x00000001)
SelectCurve(3)

'Bubbles(curve,symbol,source,size_lo,size_hi,color_lo,color_hi|,low,high,options!)

ColumnsAre(0,4,5,6)
FileAppend("test-map.dat")
Bubbles(3,954,4,100,900,0,0,,167777215,167777215)

Scale data

SelectCurve(1)
EditOperateX("x+y\times\sqrt{3.0}/2.0/1.7")
EditOperateY("-y\times2.0/\sqrt{3.0}")
SelectCurve(2)
'EditOperateY("\sqrt{y}")
'EditOperateX("x-y")
SelectCurve(3)
\begin{verbatim}
EditOperateX("x+y*sqrt(3.0)/2.0/1.7")
EditOperateY("-y*2.0/sqrt(3.0)")
SelectCurve(4)
'EditOperateY("sqrt(y)")

'ManualScale(xlo,ylo,xhi,yhi,ylo2,yhi2)
ManualScale(0,-3.0,3.0,0.5,0,0)
GridLines(2)
YAxisLabel(""
XAxisLabel(""

Legend(1,"Model")
Legend(3,"Experiment")
'*** Don't Display numbers on axis
NumberFormat(1,12,0,0,)
NumberFormat(0,12,0,0,)
Linetype(-1,3)
Color(-1,0,0,0)
'*** Solid Lines from Bulk ***
Linetype(5,1)
FunctionOfXY1Y2("0",0,2.4,0.5)
Linetype(6,1)
FunctionOfXY1Y2("-1.16",0.5,2.7,0.5)
Linetype(7,1)
FunctionOfXY1Y2("-X/sqrt(3.0)*2.0*1.95",0.0,1.05,0.01)
FunctionOfXY1Y2("-X/sqrt(3.0)*2.0*1.95+2.25",1,2.0,0.1)
FunctionOfXY1Y2("-X/sqrt(3.0)*2.0*1.95+4.5",1.995,2.65,0.25)
FunctionOfXY1Y2("X/sqrt(3.0)*2.0*2.05-2.37",0.53,1,0.01)
FunctionOfXY1Y2("X/sqrt(3.0)*2.0*2.05-4.73",1.02,2.0,0.01)
LineWidth(-2,20)
'*** These are the 6-fold symbols ***
SelectCurve(12)
SymbolType(12,266)
XY(1,0)
SelectCurve(13)
SymbolType(13,266)
XY(2,0)
\end{verbatim}
XY(2.25,-0.57)

Legend(5,"")
Legend(6,"")
Legend(7,"")
Legend(8,"")
Legend(9,"")
Legend(10,"")
Legend(11,"")
Legend(12,"")
Legend(13,"")
Legend(14,"")
Legend(15,"")
Legend(16,"")
Legend(17,"")
Legend(18,"")
Legend(19,"")
Legend(20,"")
Legend(21,"")
Legend(22,"")
Legend(23,"")
Legend(24,"")
Legend(25,"")

TextNoteLeader(200,150,50)
TextNoteEx(" ",0.2,-1.82,0x0050,,,0.5,-1.91,)
TextNoteEx(" ",0.23,-2.23,0x0010,,,,,)

' Set text for notes
TextFont(7,13,900,,,,,"Times New Roman")
TextNoteEx("(10) ",0.5,-1.84,0x0010,0.38,-2.275,)
TextNoteEx("(01) ",0.23,-1.725,0x0050,0.38,-2.275,)

' Label Si-Bragg spots
TextNoteEx("(1,0) ",0.95,0.25,0x0010,0.35,-2.23,0x0010,)
TextNoteEx("(2,0) ",1.95,0.25,0x0010,0.35,-2.23,0x0010,)
TextNoteEx("(3,0) ",2.95,0.25,0x0010,0.35,-2.23,0x0010,)
TextNoteEx("(0,1) ",0.35,-1.14,0x0010,0.85,-2.28,0x0010,)
TextNoteEx("(0,2) ",0.85,-2.28,0x0010,0.85,-2.28,0x0010,)

ManualScale(0,-2.5,2.75,0.5,0,0 )

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Appendix C

In-plane Diffraction Data

This appendix contains the in-plane diffraction data collected on the stable Pb/Si(111)7x7 wetting layer. The data was obtained after the stable wetting layer was prepared, and quenched to -45°C. The H.K columns are multiplied by 7, which is a convention used only by the author. The unmodified form factor taken directly from integrations of transverse data is the next column. The geometry corrected form factor is the final column.
| H*7 | K*7 | |F|(raw) | |F|(corrected) |
|-----|-----|-------|--------|-------------|
| 0   | 6   | 0.101746748 | 0.123090981 |
| 0   | 8   | 0.226383797 | 0.282246407 |
| 0   | 9   | 0.097603932 | 0.124588985 |
| 0   | 10  | 0.04750079  | 0.076308319 |
| 0   | 11  | 0.033489232 | 0.051688625 |
| 0   | 12  | 0.051665966 | 0.0917827 |
| 0   | 13  | 0.135987183 | 0.267228917 |
| 0   | 15  | 0.099969337 | 0.19915962 |
| 0   | 17  | 0.053007941 | 0.119825333 |
| 0   | 18  | 0.024481376 | 0.056010366 |
| 0   | 23  | 0.019215486 | 0.04611605 |
| 0   | 24  | 0.015169143 | 0.043839084 |
| 0   | 25  | 0.014150095 | 0.04204897 |
| 1   | 5   | 0.024563208 | 0.022522489 |
| 1   | 6   | 0.170415881 | 0.164128798 |
| 1   | 7   | 0.530682672 | 0.631206417 |
| 1   | 8   | 0.065819957 | 0.081513883 |
| 1   | 9   | 0.03069006  | 0.052864558 |
| 1   | 12  | 0.00377558  | 0.007093049 |
| 1   | 13  | 0.064065541 | 0.139546554 |
| 1   | 14  | 0.1247935  | 0.251919318 |
| 1   | 15  | 0.073005653 | 0.16096052 |
| 1   | 16  | 0.027297597 | 0.06141067 |
| 1   | 17  | 0.00681009  | 0.012845384 |
| 1   | 17  | 0.00681009  | 0.012845384 |
| 1   | 20  | 0.013863562 | 0.03825902 |
| 1   | 21  | 0.022939144 | 0.067297826 |
| 1   | 23  | 0.007816125 | 0.023788302 |
| 2   | 2   | 0.027509146 | 0.021998187 |
| 2   | 3   | 0.008205871 | 0.005842215 |
| 2   | 5   | 0.085395486 | 0.089655534 |
| 2   | 7   | 0.136008496 | 0.146025421 |
| 2   | 12  | 0.026248255 | 0.037420138 |
| 2   | 14  | 0.064657935 | 0.123428032 |
| 2   | 15  | 0.00562685  | 0.008239022 |
| 2   | 15  | 0.00562685  | 0.008239022 |
| 2   | 19  | 0.012931587 | 0.028244864 |
| 2   | 21  | 0.022890492 | 0.059920156 |
| 3   | 1   | 0.023200099 | 0.014575578 |
| 3   | 4   | 0.053626862 | 0.051561295 |
| 3   | 7   | 0.0405703  | 0.058047652 |
| 3   | 8   | 0.016452449 | 0.024889335 |
| 3   | 11  | 0.008367313 | 0.017893657 |
| 3   | 14  | 0.024563208 | 0.060302147 |
| 3   | 21  | 0.015873051 | 0.044595576 |
| 4   | 0   | 0.036709919 | 0.01912202 |
| 4   | 1   | 0.090958267 | 0.005220544 |
| 4   | 7   | 0.010600747 | 0.009242684 |
| 4   | 10  | 0.019250265 | 0.02667196 |
| 5   | 2   | 0.012130904 | 0.01139981 |
| 5   | 7   | 0.028094598 | 0.046310791 |
| 5   | 9   | 0.009033618 | 0.021855877 |
| 5   | 21  | 0.009630922 | 0.028072593 |
| 6   | 2   | 0.012130904 | 0.01139981 |
| 6   | 7   | 0.037633659 | 0.053269019 |
| 6   | 8   | 0.054242831 | 0.080787351 |
| 6   | 9   | 0.024851985 | 0.044992547 |
| 6   | 10  | 0.009837077 | 0.012620683 |
| 6   | 10  | 0.009837077 | 0.012620683 |
| 6   | 14  | 0.019308091 | 0.039330093 |
| 6   | 15  | 0.058844642 | 0.145186539 |
| 6   | 16  | 0.016411741 | 0.038626031 |
| 6   | 17  | 0.005085694 | 0.013092554 |
| 6   | 18  | 0.004861543 | 0.012995184 |
| 6   | 21  | 0.016681246 | 0.046205931 |
| 7   | 8   | 0.129546709 | 0.234392672 |
| 7   | 9   | 0.117083364 | 0.236991709 |
| 7   | 10  | 0.054222275 | 0.110178188 |
| 7   | 11  | 0.015844932 | 0.035480223 |
| 7   | 12  | 0.00664437  | 0.013676776 |
| 7   | 13  | 0.022792878 | 0.061515531 |
| 7   | 14  | 0.047015997 | 0.115975463 |
| 7   | 15  | 0.078968139 | 0.208529634 |
| 7   | 16  | 0.007161189 | 0.018957239 |
| 7   | 17  | 0.018899593 | 0.052991888 |
| 7   | 18  | 0.012635072 | 0.038738381 |
| 7   | 21  | 0.025863174 | 0.080974601 |
| 7   | 22  | 0.012862434 | 0.038775831 |
| 8   | 8   | 0.188029604 | 0.339327846 |
| H*7 | K*7 | |F|(raw)    | |F|(corrected) |
|-----|-----|----------------|------------------|
| 8   | 9   | 0.033449261    | 0.075941308      |
| 8   | 10  | 0.016734626    | 0.033854888      |
| 8   | 11  | 0.007406086    | 0.018238198      |
| 8   | 14  | 0.017541258    | 0.041120207      |
| 8   | 15  | 0.026694672    | 0.070069133      |
| 8   | 16  | 0.027991236    | 0.073986413      |
| 8   | 17  | 0.012457354    | 0.033952259      |
| 8   | 20  | 0.007929499    | 0.022327748      |
| 9   | 14  | 0.014055233    | 0.036865876      |
| 9   | 15  | 0.022802658    | 0.066361573      |
| 10  | 14  | 0.014181575    | 0.033630188      |
| 10  | 15  | 0.007406086    | 0.021189265      |
| 11  | 14  | 0.006474409    | 0.018065927      |
| 13  | 14  | 0.00749586     | 0.018260668      |
| 14  | 15  | 0.013068796    | 0.0381991        |
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Vita

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