Structural Characterization of Tetracene Films by Lateral Force Microscopy and Grazing-Incidence X-Ray Diffraction

by

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A Thesis
presented to
The University of Guelph

In partial fulfilment of requirements
for the degree of
Doctor of Philosophy
in
Physics

Guelph, Ontario, Canada

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Organic semiconductors show promise to yield a novel class of bendable electronic devices, and much research efforts have focused on the optimization of these films for device performance. It is well known that the structure of organic films has a large influence over the electronic properties. In particular, the carrier mobility is often highly anisotropic, and domain boundaries have a detrimental effect on charge transport. Therefore the domain structure and lattice orientation are of particular interest. However, little is known about the domain structure of organic films, and techniques to study these properties have only begun to emerge in recent years.

In this thesis, we apply two experimental techniques, Grazing-Incidence X-ray Diffraction (GIXD) and Lateral Force Microscopy (LFM), toward studying the lattice and domain structure of tetracene films grown on the silicon(001)-monohydride surface. We describe the necessary steps toward optimizing the sensitivity of these techniques to the domain structure. Results show that the crystalline tetracene films form a layered morphology in which the a-b plane lies parallel to the substrate surface. The film lattice structure is similar to bulk tetracene, and the lattice is confined to two orthogonal orientations, forming a partially-commensurate relationship with the
substrate surface lattice along the film $\vec{a}$ axis. LFM images reveal two types of polycrystalline domains. The first type ("major domains") are tens of microns in size, and are classified by their lattice orientation. They are subdivided into the second type ("sub-domains"), which range from 0.1 to 5\(\mu\)m in size, and are argued to represent regions of uniform molecular tilt direction. The GIXD data show that the single-crystal domains which comprise these two larger domain types are anisotropic in size, being up to two times longer along the film $\vec{b}$ axis than along $\vec{a}$. The single-crystal domains range from 0.05 to 0.2\(\mu\)m in size, depending on lattice orientation and film thickness. The mathematical basis for these single-crystal domain size calculations is presented. The single-crystal domain sizes are thickness-dependent, and are two orders of magnitude smaller than a typical surface island observed in atomic-force microscopy (AFM) topographs. Substrate steps can also significantly influence the film structure by inducing boundaries in the single-crystal domains and sub-domains, but not in the major domains. This detailed knowledge of the domain structure of organic thin-films may assist in our understanding of the factors which affect charge transport in thin films, and may help to direct research efforts in optimizing the film structure for device performance.
Acknowledgements

I would foremost like to thank my advisor, Professor Xiaorong Qin, for the opportunity she has provided me as a graduate student, and for her support during my time at the University of Guelph. Through her guidance, I was able to make significant advances in the development of my skills as a scientific researcher and writer.

I owe significant thanks also to Professor Detong Jiang for allowing me to benefit from his extensive experience in the areas of synchrotron radiation and associated technology. He has allowed me a rare opportunity to work directly with this truly fascinating and powerful research tool, which has added a crucial and enlightening dimension to my thesis work.

I would also like to thank the members of my advisory, Prof. John Dutcher, Prof. Elisabeth Nicol, and Prof. Dan Thomas, for their time and efforts in attending my committee meetings over the years, and for reviewing my thesis. Their comments have helped to provide direction in my research projects. I also thank the members of my examination committee, Prof. Jun Nogami (University of Toronto), Prof. Paul Rowntree, and Prof. Rob Wickham for their insightful questions and comments regarding my thesis work.

I would like to acknowledge the following beamline scientists who provided technical assistance during the synchrotron experiments: From the Advanced Photon Source in Chicago, Illinois; Robert Gordon and Qunfeng Xiao, and from the Canadian Light Source in Saskatoon, Saskatchewan; Chang-Yong Kim, Ning Chen, and Tom Regier. Thanks also to Prof. James Britton (McMaster University) for insightful discussions during the early stages of the X-ray experiments in this thesis.

I would also like to acknowledge the many good friends I made during my time
at the University of Guelph who have enriched my experience here, including, but
not limited to; Marc Bergevin, Brent Preston, Mike Arthurs, Cathy Fan, Lin Chen,
Dan Glickman, Ian MacKay, Shun Lu, Thamara Laredo, Bryan Holland, Taylor Bin-
nington, Kevin Miller, Zach Arthur, Mostaffa Nategholeslam, May Lee, Shaqa Vafaei,
Adam Raegen, Meaghan Ward, Chris Heirwegh, and Russell Spencer. Thanks also to
my former colleague, Dr. Jun Shi, for his company for several years in the lab, and
for carrying out the necessary preliminary work in optimizing the system and film
growth conditions which made my thesis project possible.

Finally, I would like to give thanks to my family for their support throughout my
student career, and especially to my wife, Marina, for her never-ending love, support
and encouragement.

The work presented here was supported by the Natural Sciences and Engineer-
ing Research Council (NSERC) of Canada, the Canadian Foundation for Innovation
(CFI), and by the Ontario Innovation Trust (OIT). Use of the HXMA beamline at
the Canadian Light Source (CLS) was supported by NSERC, the National Research
Council (NRC) of Canada, the Canadian Institutes of Health Research (CIHR), and
by the University of Saskatchewan. Use of the PNC/XOR facilities at the Advanced
Photon Source (APS) was supported by the U.S. Department of Energy, Office of Sci-
ence, Office of Basic Energy Sciences, under contract number DE-AC02-06CH11357,
and by a major facilities access grant from NSERC.
Contents

Title Page i

Abstract ii

Acknowledgements iv

Contents vi

List of Tables xi

List of Figures xii

1 Introduction 1

1.1 Organic Semiconductors ............................................. 1
1.2 Tetracene ............................................................ 5
1.3 The Si(001)-Monohydride Surface .................................... 9
1.4 Molecular Beam Deposition in a Vacuum Chamber ............... 11
1.5 Summary of Past Work, and Motivation of the Thesis .......... 12
1.6 Outline of the Thesis ............................................... 16
## 2 Atomic Force Microscopy

2.1 Basic AFM Theory and Operation .................................. 19
2.2 Lateral Force Microscopy ............................................. 23
2.3 Experimental Details .................................................. 25
   2.3.1 Adjusting the Sample Orientation ............................... 25
   2.3.2 The Imaging Force ............................................... 27
   2.3.3 Calibration of the Imaging Force ............................... 27
   2.3.4 Multi-Channel Image Acquisition .............................. 28

## 3 Grazing-Incidence X-ray Diffraction: Experimental Details

3.1 Experimental Apparatus and Equipment ............................. 30
   3.1.1 Synchrotron Facilities .......................................... 31
   3.1.2 The GIXD Apparatus ............................................ 32
3.2 GIXD Experimental Procedures ...................................... 41
   3.2.1 Optimizing the Diffracted Intensity ........................... 41
   3.2.2 Optimizing the In-Plane Resolution in Reciprocal-Space .... 43
   3.2.3 Data Collection Procedure .................................... 56
3.3 Data Processing ....................................................... 61
   3.3.1 Reciprocal-Space Mapping .................................... 61
   3.3.2 Correcting for Instrumental Peak Broadening (Deconvolution) 62

## 4 Characterization of the Film Structure by GIXD

4.1 Sample Preparation .................................................... 73
4.2 Lattice Structure and Lattice Orientation .......................... 74
   4.2.1 Determination of the Film Lattice Orientation by GIXD ..... 74

vii
4.2.2 The In-Plane Lattice Parameters, and Partial Commensurability with the Substrate ........................................ 82

4.3 Diffraction-Peak Profile Analysis ........................................... 84

4.3.1 Diffraction-Peak Intensity Profile for a Single Crystallite .... 84

4.3.2 Peak Width versus Crystallite Size (The Scherrer Equation) . 92

4.3.3 Diffracted Intensity from Multiple Crystallites ................. 96

4.4 GIXD Determination of Single-Crystal Domain Sizes and Preferred Growth Direction ........................................... 104

4.5 GIXD of Tetracene Films on High Step-Density Substrates ........ 110

4.5.1 Effect of Substrate Steps on Single-Crystal Domain Sizes .... 110

4.5.2 Step-Induced Single-Crystal Domain Boundaries ............... 113

4.5.3 Step Influence on Single-Crystal Domain Shape and Growth Anisotropy .................................................. 113

4.6 Chapter Summary ............................................................... 116

5 Real-Space Imaging of the Film Domain Structure by Lateral Force Microscopy ......................................................... 119

5.1 Observation of Major Domains in the TSM Images ............... 120

5.1.1 Dependence of the Major-Domain Contrast on Scan Direction 122

5.1.2 Effect of the Major Domains on Island Orientation ............ 128

5.1.3 Physical Interpretation of the Major Domains ................. 128

5.1.4 TSM Contrast Mechanism of the Major Domains ............ 131

5.1.5 Polycrystallinity of the Major Domains ......................... 132

5.2 Observation of Sub-Domains in the TSM and FFM Images ....... 133

5.2.1 Dependence of the Sub-Domain Contrast on Scan Direction . 135
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.2 Physical Interpretation of the Sub-Domains</td>
<td>135</td>
</tr>
<tr>
<td>5.2.3 Polycrystallinity of the Sub-Domains</td>
<td>142</td>
</tr>
<tr>
<td>5.2.4 Elongation of the Sub-Domains</td>
<td>144</td>
</tr>
<tr>
<td>5.3 Domain Structure of the First and Second Film Layers</td>
<td>144</td>
</tr>
<tr>
<td>5.4 Influence of Substrate-Steps on the Domain Structure</td>
<td>147</td>
</tr>
<tr>
<td>5.5 Chapter Summary</td>
<td>153</td>
</tr>
<tr>
<td>6 Conclusion</td>
<td>155</td>
</tr>
<tr>
<td>6.1 Summary of Results</td>
<td>155</td>
</tr>
<tr>
<td>6.2 Future Work</td>
<td>157</td>
</tr>
<tr>
<td>Bibliography</td>
<td>160</td>
</tr>
<tr>
<td>A X-Ray Diffraction: Background and Theory</td>
<td>168</td>
</tr>
<tr>
<td>A.1 Overview of X-Ray Diffraction Theory</td>
<td>169</td>
</tr>
<tr>
<td>A.1.1 Diffraction from Two Scattering Points</td>
<td>169</td>
</tr>
<tr>
<td>A.1.2 Diffraction from a Crystal</td>
<td>170</td>
</tr>
<tr>
<td>A.1.3 The Reciprocal Lattice</td>
<td>174</td>
</tr>
<tr>
<td>A.1.4 The Structure Factor and Atomic Form Factor</td>
<td>177</td>
</tr>
<tr>
<td>A.1.5 The Scattering Cross-Section</td>
<td>183</td>
</tr>
<tr>
<td>A.2 Diffraction from a Thin Film</td>
<td>188</td>
</tr>
<tr>
<td>A.2.1 Crystal Truncation Rods</td>
<td>188</td>
</tr>
<tr>
<td>A.2.2 The Index of Refraction for X-rays</td>
<td>190</td>
</tr>
<tr>
<td>A.2.3 The Critical Angle for Total External Reflection</td>
<td>196</td>
</tr>
<tr>
<td>A.2.4 Behaviour of the Evanescent Wave near the Critical Angle</td>
<td>200</td>
</tr>
</tbody>
</table>
List of Tables
1.1

The lattice parameters of tetracene. . . . . . . . . . . . . . . . . . . .

4.1

Comparison of lattice parameters for the thin-film phase of tetracene
with that of the bulk structure. . . . . . . . . . . . . . . . . . . . . .

4.2

8

83

Table of single-crystal domain-size measurements for tetracene films of
various thickness grown on 0.03◦ miscut Si(001) substrates. . . . . . . 108

4.3

Table of single-crystal domain-size measurements for tetracene films
grown on high step-density, 0.3◦ miscut Si(001) substrates. . . . . . . 111

E.1 Table of calculated intensities for the lowest-order in-plane diffraction
peaks of bulk tetracene. . . . . . . . . . . . . . . . . . . . . . . . . . 229

xi


List of Figures

1.1 Example of the layout of an organic field-effect transistor. . . . . . . 3
1.2 Tetracene molecular and lattice structure. . . . . . . . . . . . . . . . 6
1.3 Definitions of the lattice parameters used to describe the dimensions
of a unit cell. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 7
1.4 Illustration and STM image of the clean Si(001) surface. . . . . . . . 10
1.5 STM image of a tetracene film grown on a Si(001)-monohydride substrate. 13

2.1 Schematic diagram illustrating the basic principles of AFM operation. 20
2.2 Photographs of the AFM probe assembly and the four-segment pho-
todetector used in the AFM experiments. . . . . . . . . . . . . . . . . 22
2.3 Illustration of the difference between the FFM and TSM modes of
operation. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 24
2.4 The sample holder used to adjust the sample orientation in the AFM
experiments. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 26
2.5 Plot of AFM deflection signal vs. cantilever height. . . . . . . . . . 29

3.1 The basic geometry of the GIXD experiment. . . . . . . . . . . . . 33
3.2 Schematic diagram of the main components of the GIXD apparatus. . 34
3.3 Some segments of the experimental apparatus at the APS. . . . . . . 36
3.4 Schematic diagram of the Huber Diffractometer used in the GIXD experiments. .............................. 37
3.5 Photographs of the Huber Diffractometers used for the GIXD experiments. .............................. 38
3.6 Photographs of the vacuum chamber at the APS. ............... 40
3.7 Using a phosphor screen to observe the incident and reflected beams, and the process used to determine the critical angle. ............... 44
3.8 Illustration of the relationship between the in-plane diffractometer angles and $\vec{Q}$. .............................. 46
3.9 The two dominant sources of spread in the angular resolution of $\delta$, the azimuthal exit angle of the diffracted beam. ............... 48
3.10 Visualization of the relation between the spread in the diffractometer angles, and the size of the sampling window in reciprocal-space. .... 53
3.11 Visualization of the diffraction process in reciprocal-space. ............... 58
3.12 Example of mapping from diffractometer angles to reciprocal-space coordinates. .............................. 63
3.13 Reciprocal-space map of the silicon substrate (111) peak which was used as an estimate for the point-spread function. ............... 66
3.14 Examples of applying the deconvolution procedure to the data. ............... 69

4.1 Large-scale AFM topograph of a 4ML tetracene film grown on an atomically flat Si(001)-monohydride surface. .............................. 75
4.2 A sample of the data collected during the peak-searching process. .... 77
4.3 Two-dimensional reciprocal-space map of measured diffraction peaks for a 4ML tetracene film. .............................. 79
4.4 Illustration of the two possible film-substrate orientations that were detected in the GIXD data. ........................................ 81

4.5 A parallelepiped-shaped crystal with its axes oriented parallel to the \( \hat{a}, \hat{b}, \) and \( \hat{c} \) directions. ........................................ 89

4.6 Example of a diffraction pattern of concentric shells formed by revolving each \( hkl \) diffraction peak about the origin. ......................... 95

4.7 A collection of crystallites with identical lattice orientations. ........ 98

4.8 An intuitive explanation for the preference of a single-crystal domain to grow along the \( \vec{b} \) direction. .............................. 106

4.9 AFM topographs of a 4ML tetracene film grown on a low step-density Si(001)-monohydride surface, and a high step-density surface. .... 112

4.10 Two-dimensional reciprocal-space map of measured GIXD peaks for a 4ML tetracene film grown on a high step-density surface. .......... 115

4.11 Schematic illustrations of a possible step-density influence on the domain formation. ................................................... 117

5.1 AFM topograph and corresponding TSM image of a 4ML tetracene film grown on a 0.03° miscut Si(001) surface. ......................... 121

5.2 TSM images of a particular location on a 4ML tetracene film grown on 0.03°-miscut Si(001). ................................................. 123

5.3 TSM images demonstrating the inversion of contrast that occurs during backward scanning. .................................................. 125

5.4 Illustration of the relation between twist signals obtained during forward or backward scanning. .............................................. 126
5.5 Two TSM hysteresis images of the same film location, but with different
TSM scan directions. .......................................................... 129
5.6 AFM topograph (left) and corresponding TSM image (right) demonstrat-
ing the effect of the major domains on island orientation. ........ 130
5.7 AFM topograph and LFM images revealing the presence of sub-domains
in the tetracene films. ....................................................... 134
5.8 FFM and TSM images showing the dependence of the sub-domain
contrast on scan direction. ............................................. 136
5.9 A proposed interpretation of the sub-domains, in which different do-
mains are produced by simple 180° rotations about the \( \vec{a} \) or \( \vec{b} \) axes, or
about the surface normal. .................................................. 138
5.10 Illustration of the proposed mechanism by which domains of different
molecular tilt can be observed in the FFM images. ................. 140
5.11 The proposed mechanism by which domains of different molecular tilt
can be observed in the TSM images. ................................. 143
5.12 AFM and LFM images of the first and second tetracene layers. .... 146
5.13 High-resolution AFM topograph and TSM image revealing that the
sub-domain boundaries conform to the steps in many places. ...... 149
5.14 TSM image demonstrating the effect of substrate steps on sub-domain
shape anisotropy. ................................................................. 151
5.15 Comparison of major domains in TSM images of 4ML films grown on
low step-density (left) and high step-density (right) substrates. .... 152

A.1 The geometry of the scattering process from two scattering points. . 171
A.2 A rectangular crystal lattice with lattice planes. ...................... 176
A.3 Light scattering from a single, free electron. . . . . . . . . . . . . . . 178
A.4 A numerical plot of the dependence of the atomic form factor $f(\vec{Q})$ on
the Bragg angle $\theta$ for the 1s state of a hydrogen atom . . . . . . . . 184
A.5 A conceptual model for the definition of the electron cross-section for
X-ray scattering. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 185
A.6 Schematic illustration of the reciprocal-space diffraction pattern for a
thin, two-dimensional crystal. . . . . . . . . . . . . . . . . . . . . . . . 191
A.7 Illustration of the refraction process in a layer of free electrons. . . . 192
A.8 Definition of the variables in the Fresnel Equations (A.43). . . . . . . 198
A.9 Plots of the variation of transmission coefficient, X-ray penetration
depth, and transmission angle with incident beam angle. . . . . . . . 202
B.1 Labelling convention for the diffractometer angles. . . . . . . . . . . . 205
B.2 Definitions of the angles used to position the X-ray detector with re-
spect to the incident beam. . . . . . . . . . . . . . . . . . . . . . . . . 207
B.3 Definition of the zero-positions for the sample-manipulating diffrac-
tometer circles. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 210
D.1 Illustration of the procedure for vertically aligning the diffractometer
with the X-ray beam. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 223
D.2 An iterative process for positioning the sample in the middle of the
X-ray beam with its surface parallel to the beam. . . . . . . . . . . . . 226
E.1 Maple-generated plot of the atoms in the tetracene unit cell. . . . . . . 233
Chapter 1

Introduction

1.1 Organic Semiconductors

As a result of intense research efforts over the past two decades, significant advances have been made toward the development of organic semiconducting materials for use in electronics applications [1–6]. These materials possess characteristics not associated with conventional inorganic semiconductors such as silicon. For example, they are mechanically flexible [3, 4, 7], and can therefore be used to make bendable electronic devices. They can also be processed at lower temperatures compared with inorganic semiconductors [1, 2], and hence can be used on a wider variety of substrates. Furthermore, a variety of fabrication techniques have been developed which allow large-area devices to be made at low cost [3, 5, 8–11]. Due to these properties, organic semiconductors are envisioned as alternatives to inorganic semiconductors for applications in which these characteristics are desirable. To date, organic semiconductors have shown potential for use in applications such as organic field-effect transistors (OFETs) [2, 5, 6, 12], organic light-emitting diodes (OLEDs) and light-emitting tran-
sistors (OLETs) [13–18], flexible electronic displays [3, 19–23], solar cells [24, 25], and radio-frequency identification cards [26, 27].

Organic semiconductors are materials made of organic molecules which have semiconducting properties in their solid form [28, 29]. They can be broadly classified into two groups [4]: Polymers are long molecules which are generally considered easy to process, but possess poor electrical characteristics due to a high degree of disorder in the material. On the other hand, oligomers are small molecules which easily form highly-ordered crystal structures, and hence tend to have better electrical properties than polymers, but are typically harder to handle and fabricate into devices. For the purposes of this thesis, the remainder of this discussion will focus on oligomers.

The fabrication of devices such as OFETs generally requires the deposition of a film of the organic material onto a substrate [6, 30]. An example of the layout of such a device is shown in figure 1.1, in which an organic semiconductor is used as the active layer. When a suitable voltage is applied to the gate electrode, charge carriers accumulate in the organic semiconductor layer (organic semiconductors usually exhibit p-type behaviour [2, 5, 31], in which case a negative gate-voltage is applied), allowing a current to pass between the source and drain electrodes.

Very frequently, the performance of an organic semiconducting material is gauged by the charge carrier mobility ‘μ’ of the material [30], since the mobility directly affects the transistor switching speed. Thus far, π-conjugated molecules which, in their crystal form, exhibit significant overlap in the π-orbitals between adjacent molecules, have been considered to be promising candidates for high-performance, organic electronic devices [2, 5, 32]. The orbital overlap allows for charge transport to occur via a band-like or hopping mechanism [2, 31, 33, 34].
Figure 1.1: Example of the layout of an organic field-effect transistor. When a suitable voltage is applied to the gate electrode, charge carriers accumulate in the organic semiconductor layer, allowing a current to pass between the source and drain electrodes.
Because of the strong dependence of the electrical properties on film structure and molecular orientation, the electronic properties of organic semiconductors often have dependencies that are not common in inorganic materials. For example, there is usually a high degree of anisotropy in the electrical properties of organic semiconductors [35–38]. It is also well-established that organic thin films tend to be polycrystalline, and therefore tend to have poorer electrical characteristics than single-crystals due to the presence of grain boundaries, which have a detrimental effect on charge transport [2,35,39–42].

As a result of these factors, film quality, morphology, and lattice structure have a large effect on the carrier mobilities of these materials, and hence potential device performance [4, 43–47]. Because of this, a significant amount of research has been devoted to the study of the growth processes of thin films, and the factors that affect film quality and ordering [4, 48–53]. Since it has been shown that conduction is usually confined to the first few molecular film layers [43, 54, 55], such studies are often restricted to thin films which are only a few molecular layers thick.

In this thesis, tetracene (a π-conjugated oligomer consisting of four fused benzene rings) grown on the silicon(001)-monohydride surface is used as a model system for fundamental film growth and structure studies. Two complementary experimental techniques (grazing-incidence X-ray diffraction (GIXD) and lateral force microscopy (LFM)) are used to reveal detailed information about the lattice and domain structure of the films. Experimental results demonstrating the effect of substrate steps on the film structure and single-crystal domain distribution are also presented.
1.2 Tetracene

Tetracene (C\textsubscript{18}H\textsubscript{12}) is an aromatic molecule consisting of four fused benzene rings (figure 1.2a). It has been shown to have good luminescent properties, and is therefore considered to be a good candidate for use in applications involving light-emitting transistors [16,17,56–58].

In their crystal form, tetracene molecules are packed in a layered, herringbone formation [59–61] as depicted in figure 1.2b and c. This formation leads to a significant amount of overlap in the $\pi$-orbitals, which mainly extend above and below the molecular plane, allowing for charge transport to occur along this direction.

In the bulk crystal form, tetracene has a triclinic unit cell. As a reference for the discussion in later chapters, the lattice parameters, as reported by Holmes and co-workers [59], are included in table 1.1 (see figure 1.3 for the conventional definitions of the lattice parameters with reference to a triclinic unit cell). Note that there is some inconsistency, in existing published literature, regarding the labelling conventions of the tetracene lattice vectors. Some works label the in-plane lattice vectors, $\vec{a}$ and $\vec{b}$, such that $\vec{a}$ is the longer of the two [61,62]. In other works, such as that by Holmes and co-workers, the in-plane lattice vectors are interchanged such that $\vec{b}$ is the longer of the two [59,63]. For the purposes of this thesis, we use the former of the two conventions in order to remain consistent with our published works [64–67]. This labelling convention is as shown in figure 1.2b and c.
Figure 1.2: a) The structure of a tetracene (C\textsubscript{18}H\textsubscript{12}) molecule. Carbon atoms are shown in black, hydrogen in white. b) View of the tetracene lattice from above the a-b plane, and c) from a view parallel to the a-b plane. The molecules are arranged in a layered herringbone formation. The positions of the molecules in the figure are based on the data reported by Holmes and co-workers [59].
Figure 1.3: Definitions of the lattice parameters used to describe the dimensions of a unit cell. The three lattice vectors are represented by $\vec{a}$, $\vec{b}$, and $\vec{c}$, and the angles between them are represented by $\alpha$, $\beta$, and $\gamma$. 
Table 1.1: The lattice parameters of tetracene, as reported by Holmes and co-workers [59]. The parameters of the unit cell are defined in figure 1.2 (see figure 1.3 for the standard definitions of the lattice parameters used in crystallography). Note that the labelling convention used by Holmes differs from that used in this thesis, and in some other published works [61, 62], in that the \( \vec{a} \) and \( \vec{b} \) axis labels are interchanged. To minimize confusion, the parameter values under both labelling conventions are given here.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>( \alpha ) (°)</th>
<th>( \beta ) (°)</th>
<th>( \gamma ) (°)</th>
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<tr>
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<td>7.8376Å</td>
<td>13.0104Å</td>
<td>77.127°</td>
<td>72.118°</td>
<td>85.792°</td>
</tr>
<tr>
<td>This Thesis</td>
<td>7.8376Å</td>
<td>6.0565Å</td>
<td>13.0104Å</td>
<td>107.882°</td>
<td>102.873°</td>
<td>85.792°</td>
</tr>
</tbody>
</table>
1.3 The Si(001)-Monohydride Surface

In the experiments to be presented here, the silicon(001)-monohydride surface is chosen as a substrate for tetracene film growth. This surface has a simple and well understood structure [68], which makes it ideal for fundamental organic film growth studies.

The clean (unpassivated) silicon(001) surface takes on a 2×1 reconstruction with a rectangular unit cell measuring 3.84Å×7.68Å [69, 70]. The rectangular structure results from the dimerization of the surface atoms, which form rows of silicon dimers as shown in figure 1.4. Atomic steps occur naturally on the surface, and separate the atomic terraces. The dimer rows on adjacent terraces are oriented in orthogonal directions, as seen in the STM image of figure 1.4b.

Each silicon dimer is held together by a covalent bond (i.e. a σ-bond). The remaining “dangling” bond of each silicon atom form a weaker π-bond. The π-bonds are normally very reactive. In order to passivate the substrate, and reduce the strength of interaction with the film, the surface is saturated with hydrogen, resulting in an atomically flat, inert silicon(001)-monohydride surface. The apparatus and procedure that are used for preparing this surface are described in section 4.1.

Due to the simple structure of the surface, and its low reactivity, it is well-suited for elucidating the processes involved in film growth. By cleaving the silicon surface at a small miscut angle, the average density and orientation of the atomic substrate steps may be controlled. This concept is used in chapters 4 and 5 to study the effects of substrate steps on film growth.
Figure 1.4: a) Illustration of the clean Si(001) surface. An overhead view of three silicon layers are shown, with the top layer atoms drawn larger and lighter. The top layer atoms dimerize, forming dimer rows. The resulting surface is a $2 \times 1$ reconstruction of the bulk-terminated structure. The directional axes indicate the lattice (110) and (1\overline{1}0) directions. b) STM image of a clean, Si(001) surface. The dimers and dimer rows are clearly seen, along with an atomic step separating two terraces with dimer rows oriented in orthogonal directions. Dimer vacancies, a type of defect, can be seen in the image.
1.4 Molecular Beam Deposition in a Vacuum Chamber

Most commonly, methods for the deposition of thin crystalline films of organic materials on solid substrates are based on deposition from a vapour or from a solution. Both methods have advantages and disadvantages [30, 46, 71]. Vapour-based methods have the advantage of forming exceptionally high-quality, well-ordered films which are suitable for high-performance devices. However, these methods usually require expensive equipment, and may be difficult to scale up to large-scale manufacturing processes. On the other hand, solution-based methods are inexpensive and scalable. However, oligomers typically have low solubility, which makes solution deposition difficult for these molecules. Furthermore, the presence of the solvent may have detrimental effects on film quality [46].

For the purposes of the experiments to be presented here, in which our objective is to shed light on fundamental film growth processes and film-substrate interactions, we favour the vapour-based approach. In particular, the films are grown by organic molecular-beam deposition (OMBD) [72]. In this approach, film-deposition is carried out in an ultra-high vacuum chamber in order to ensure that the growth process occurs in an environment that is free from impurities. A crucible containing the organic material is heated to near the sublimation temperature, at which point it begins to vapourize. The substrate is exposed to this vapour for a controlled length of time in order to grow the film to a desired thickness.

The OMBD process is simple to set up and control, and is therefore well-suited for fundamental film growth studies. Details on the film growth apparatus and procedure
1.5 Summary of Past Work, and Motivation of the Thesis

The work presented here builds upon the results of our past study [64, 73]. In that work, we employed Scanning Tunnelling Microscopy (STM), Atomic Force Microscopy (AFM), and Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy in order to characterize the structure of tetracene films grown on the silicon(001)-monohydride surface.

STM [74] is a powerful technique which is capable of imaging conductive surfaces with atomic resolution. We showed that, while high-quality images could not be obtained for films of 2 monolayers (ML) or less, images of 3ML films revealed a periodic pattern corresponding to the film lattice, as shown in figure 1.5. The lattice parameters were measured to be \( a = 7.3 \pm 0.6\,\text{Å} \) and \( b = 5.5 \pm 0.6\,\text{Å} \), which matched the a-b plane of the bulk tetracene structure (table 1.1) to within uncertainty, demonstrating that the molecules stand upright on the surface. In the images, which spanned an area of up to \( 0.1 \times 0.1\,\mu\text{m}^2 \), only two orientations of the film lattice were seen. The constrained orientation provided evidence for a partially-commensurate relationship between the film and substrate.

To complement the STM results, AFM was used to image the large-scale (up to 100\( \mu \)m) morphology of the film (for example, see figure 4.1 on page 75). Measurements of tetracene layer heights were similar to the inter-planar spacing of a-b planes in bulk tetracene, showing that the molecules stand upright on the surface, in agreement with
Figure 1.5: STM image of a tetracene film grown on a Si(001)-monohydride substrate. This image was obtained in work preceding this thesis [64,73], in which it was shown that the tetracene film lattice forms a bulk-like structure which may exist in two possible orientations. The lower-left axes indicate the substrate $[\overline{1}10]$ and $[\overline{\overline{1}}0]$ directions. The tetracene lattice orientation is indicated by the $\vec{a}$ and $\vec{b}$ vectors in the lower-right corner.
the STM results. Sub-monolayer film islands showed fractal-like branches, while in thicker films (>1ML) the islands were made up of dendritic branches. In addition, based on the tetracene layer-height measurements, the molecules in the thicker films were found to stand slightly more upright, suggesting some structural difference exists between the two film thicknesses.

NEXAFS [75] was used in order to gain further insight into the interior structure of the films, and to observe the evolution with film thickness. With this technique, it was possible to directly measure the average angle between the molecular plane normal and the substrate surface normal. A change in this angle was detected during the initial layers of film-growth, up to about 3ML, after which it remained roughly constant at the value expected for bulk tetracene. This provided further evidence for the structural transition that was detected in the STM and AFM results.

While the STM experiments showed that the films were composed of domains of two lattice orientations, only the localized structure could be seen, and no long-range information on the domain structure was available. On the other hand, the AFM topographs could reveal long-range morphology data, however this technique was insensitive to the internal structure of the films. As mentioned previously in section 1.1, the internal structure, including the domain size and shape distribution, are of particular interest due to the effect of domain boundaries and lattice orientation on charge transport properties. Despite this well-acknowledged importance, techniques for studying the domain structure of organic films have only begun to emerge within the past few years [76], and therefore few experimental studies have addressed the domain structure properties. In the present work, we endeavour to address these issues through the use of two techniques; Grazing-Incidence X-ray Diffraction (GIXD) and
Lateral Force Microscopy (LFM).

When conducted with intense synchrotron radiation, GIXD can be made sensitive to surface characteristics (see chapter 3 and appendix A). By measuring the reciprocal-space positions of diffraction peaks, the lattice parameters can be measured to far better accuracy than with STM, and we may also obtain details on the preferred lattice orientations and registration relative to the substrate. Furthermore, the intensity profiles of the diffraction peaks are related to the size and shape of the single-crystal domains that make up the film, and can thus be used to study these properties. Because of these advantages, GIXD was chosen as a suitable technique for studying the single-crystal domain structure of the films.

While GIXD yields rich information through analysis in reciprocal-space, it provides no direct real-space information on the domain distribution. Furthermore, while information on the size and shapes of the single-crystal domains can be obtained, GIXD can not be used to detect longer-range ordering beyond the single-crystal domain boundaries, or to determine whether correlations exist between nearby single-crystal domains themselves. Therefore LFM was selected as a complementary experimental technique. LFM can be operated in two modes: Transverse Shear Microscopy (TSM) has recently been shown to be sensitive to the lattice orientation in thin organic films [77–82], while Frictional Force Microscopy (FFM) is sensitive to frictional properties which can in some cases reflect molecular orientation [83–86]. Therefore, LFM was used to obtain real-space information on the long-range ordering that GIXD could not provide.
1.6 Outline of the Thesis

We begin in chapter 2 by providing relevant background and theory of operation for AFM. The adaptation of conventional AFM to LFM is then described in order to provide a basis for an understanding of the experimental results presented in later chapters. Details on the equipment and procedures used in these experiments are also provided.

Chapter 3 presents the experimental details for the GIXD experiments. The most important components of the apparatus are described, and the details for the setup and optimization of the diffraction experiments are given. The essential aspects of data processing, including mapping of the data to reciprocal-space, and correcting of instrumental peak-broadening, are also described. For convenient reference, a summary of the relevant background and theory of X-ray diffraction is included in appendix A.

Chapters 4 and 5 present the experimental results of the GIXD and LFM experiments. Beginning in chapter 4, the GIXD data is presented. It is shown how this data is analyzed to reveal detailed information on the lattice structure of the tetracene films and preferred lattice orientations. By analyzing diffraction-peak intensity profiles, details are obtained of the sizes and dimensions of the single-crystal domains which comprise the polycrystalline tetracene films. Films grown on high step-density substrates are also studied in order to determine the effect of substrate steps on the single-crystals.

In chapter 5, LFM is used to obtain real-space images of the domain structure of the films that is not observable by conventional AFM. The domains are interpreted in terms of regions of uniform lattice orientation and molecular tilting, and the results are
compared to the GIXD data presented in chapter 4. Possible physical mechanisms which may be responsible for the contrast in the LFM images are discussed. The influence of substrate steps on these domains is also examined.

Chapter 6 concludes the thesis by summarizing the results presented, and discussing the relevance of the findings toward understanding and optimizing the structure and performance of organic semiconductor films for potential organic semiconductor devices. Some suggestions for future work and research directions are discussed.
Chapter 2

Atomic Force Microscopy

The *atomic force microscope* (AFM), first reported in 1988 [87], has become an important tool in surface science [88]. This experimental technique allows the acquisition of real-space images of a surface under study with, in the best cases, up to atomic resolution [89]. Compared to its predecessor, the scanning tunnelling microscope, the AFM offers the advantage of the ability to image insulators as well as conductors and semiconductors, and is capable of many modes of operation [88, 90].

In the experiments presented in this thesis, AFM imaging is used to provide real-space information to complement the structural information offered by X-ray diffraction. Using the less conventional *lateral force* mode of AFM operation, imaging of the crystal domains is achieved. This chapter describes the basics of AFM operation, with a special focus on the modes of operation used in this thesis. The experimental setup and procedures are also described.
2.1 Basic AFM Theory and Operation

A basic AFM typically makes use of a conical tip mounted to the end of a flexible cantilever, illustrated in figure 2.1a, to probe a surface. As the tip moves along a surface of study, the deflection of the cantilever is monitored in order to form a rasterized topographic image of the surface. The cantilever is usually very thin, so as to allow it to flex very easily when a very small force is applied. Typical dimensions for the cantilevers used in the present work are 200-400µm long, by 40-50µm wide, and by 1-2µm thick.

During AFM operation, a laser beam is directed at the reflective surface of the cantilever, and allowed to reflect onto a position-sensitive detector, as illustrated in figure 2.1a. Small deflections in the cantilever will cause small deviations in the reflected laser beam, shown in figure 2.1b, which are measured by the detector. The position-sensitive detector is divided into four quadrants, each consisting of a sensitive photodetector. The position of the laser beam is determined by the differences in the signals measured by the four segments. Vertical deflections of the cantilever result in movement of the laser between the top and bottom halves of the detector, while twisting motions of the cantilever cause the laser to deviate between the left and right halves. The two types of measurements can be monitored simultaneously during image acquisition.

Shown in figure 2.2a is the AFM probe assembly used in the present study, in which the major components are schematically labelled. The probe consists of a head on which the cantilever is mounted, a piezoelectric transducer which controls the nanoscopic motions of the cantilever along three orthogonal directions, and a laser and photodetector used to detect deflections of the cantilever. The four-segment
Figure 2.1: Schematic diagram illustrating the basic principles of AFM operation. 
a) As the tip moves across the surface, small deflections in the cantilever due to the 
changing topography of the surface result in movement of the reflected laser beam. 
The changes in beam position are measured by a four-segment photodetector. b) 
Vertical deflections of the tip result in motion of the laser beam between the upper 
and lower segments of the detector, while twisting motions of the cantilever result in 
motion of the laser beam between the left and right segments of the detector.
detector is shown in figure 2.2b.

While there are many possible modes of operation that can be used to obtain the AFM topographs, two of the more common and well-known modes are described here. In “contact mode”, the tip is brought into contact with the surface, resulting in a vertical deflection of the cantilever (as measured by the vertical position of the reflected laser beam). The magnitude of this deflection is maintained constant during image acquisition. The other mode is commonly known as “tapping mode”. In this mode, the cantilever is made to oscillate at or near its resonant frequency (typically a few hundred kilohertz) by applying an AC driving signal to the piezoelectric transducer. When the tip is brought close enough to interact with the surface, the interaction causes changes in both the amplitude of oscillation [91], as well as the phase shift between the driving force signal and the cantilever oscillation signal [92]. Either of these values may be used as the control variable, and held constant during image acquisition. In both modes of operation, the cantilever “height” (i.e. the distance between cantilever and the surface) is recorded during tip scanning in order to produce a rasterized topographical image of the surface.

These two modes of operation result in different tip-surface interactions, and are used in different circumstances depending on the experiment being conducted. Operation in tapping mode reduces the amount of time that the tip is in contact with the surface, and eliminates lateral forces between the tip and surface. For this reason, it is often favoured over contact mode for study of soft sample surfaces such as organic thin films in the hopes that film damage will be minimized [91]. On the other hand, the lateral forces between the tip and surface that arise during contact mode can be monitored while imaging, and can provide additional information during an
Figure 2.2: a) Photograph of the AFM probe assembly. A laser beam is reflected from the cantilever onto the four-segment detector. The position of the detector is indicated by a dotted grey outline. b) Photograph of the four-segment photodetector used in the AFM experiments.
experiment. This is the case for the tetracene films that are the subject of this thesis. This type of microscopy, called lateral force microscopy [77,78,93], is described in the following section.

2.2 Lateral Force Microscopy

Lateral force microscopy (LFM) is a special case of AFM imaging in contact mode, in which the lateral force is passively measured while the contact mode topographs are acquired.

The lateral force on the tip is measured by monitoring the left-right deflection of the laser beam on the four-segment detector. As discussed in the previous section, this left-right beam movement occurs when the cantilever twists in response to lateral forces on the tip (see figure 2.3). For this reason, the LFM images only reflect the component of the tip force that is transverse to the long axis of the cantilever.

This fact results in two possible modes of LFM operation. Following the nomenclature used by Puntambekar and co-workers [78], these two modes are referred to as Frictional Force Microscopy (FFM), and Transverse Shear Microscopy (TSM). The two modes differ only in the scan direction relative to the cantilever axis.

In FFM mode, as shown in figure 2.3, the tip is scanned in a direction perpendicular to the cantilever axis. Therefore cantilever twisting results from forces that act along the direction of tip sliding. Such forces which oppose the tip sliding motion are what are conventionally thought of as friction forces. Hence the term “frictional force” microscopy.

In TSM mode, also shown in figure 2.3, the tip is scanned in a direction that is parallel to the cantilever axis. Thus the cantilever twists in response to forces
Figure 2.3: Illustration of the difference between the FFM and TSM modes of operation. In both modes, the twisting motion of the cantilever is monitored during contact mode imaging. The twisting force arises due to the component of the lateral force between the tip and sample that is perpendicular to the cantilever long axis. In FFM mode, the scan direction is perpendicular to the cantilever axis so that forces that are parallel to the scan direction are detected. In TSM mode, the scan direction is parallel to the cantilever axis so that forces that are transverse to the scan direction are detected.
that are transverse to the direction of tip sliding. Hence the term “transverse shear” microscopy.

2.3 Experimental Details

The AFM experiments were carried out with an Agilent Technologies 5500 Scanning Probe Microscope operating in contact mode using commercially supplied silicon tips (Nanosensors PointProbe Plus [94], Silicon-SPM-Sensor. Type: PPP-CONT. Cantilever dimensions: thickness=2±1µm, length=450±10µm, width=50±7.5µm. Tip height: 10-15µm). The control software allows the specification of the scan direction relative to the cantilever axis. By suitable specification of this scan direction, the AFM may be operated in FFM or TSM mode.

2.3.1 Adjusting the Sample Orientation

In order to change the cantilever orientation relative to the sample, the sample must be rotated. To accomplish this, a custom-built rotating attachment was added to the company-provided sample holder (figure 2.4). The attachment consisted of a glass slide glued to a small cylindrical handle. Angular measurements are shown on the handle so that the sample orientation can be quantified. A teflon collar attached to the cylinder ensures that the glass slide remains flush with the sample holder while adjusting the orientation, thus protecting the fragile AFM cantilever. With this setup, the orientation of the sample can be specified with a precision of approximately ±10°, which is adequate for the purposes of the experiments here.
Figure 2.4: The sample holder used to adjust the sample orientation in the AFM experiments. The sample is mounted on a glass slide (left), which may be rotated using the handle (right). In this way, the sample orientation may be easily adjusted during the experiments.
2.3.2 The Imaging Force

An important parameter to be selected in contact-mode AFM operation is the “imaging force”. This is the force with which the tip presses down on the sample surface during imaging. If the force is too small, then the deflection signal may not be sensitive enough to changes in surface topography, which results in a noisy or unstable image. If the force is too high, the soft film can be damaged by the tip. Fortunately, this parameter is easily adjusted while imaging through the control software, and can therefore be easily optimized simply by adjusting the value until the resulting image is satisfactory in quality.

The imaging force is most conveniently measured in terms of the deflection signal that is recorded by the four-segment detector when the tip is in contact with the surface. When the tip is disengaged from the surface, the measured deflection reading represents the equilibrium position of the reflected laser beam. This reading is taken to represent zero force applied to the tip by the sample surface. After the tip is lowered and brought into contact with the surface, any motion of the cantilever will result in a deflection of the cantilever, causing a change in the deflection signal. The difference between the deflection signal during imaging (the setpoint value) and the signal when the tip is free (the zero-force value) is taken to represent the imaging force. Due to the attractive van der Waals interaction between the tip and surface, even a negative imaging force is possible.

2.3.3 Calibration of the Imaging Force

The imaging force as determined by the change in deflection signal may be roughly calibrated to yield an estimate for the actual force between the tip and surface during
imaging [95]. To obtain this measurement, the tip is first engaged with the surface, and the cantilever height is varied while the deflection signal is monitored (here, “cantilever height” refers to the vertical position of the assembly to which the cantilever is attached, and is controlled via the vertical motion of the piezoelectric transducer). This experiment yields a linear relationship as shown in figure 2.5. The slope of this line represents the rate of change of the deflection signal with cantilever height. This slope may be converted to force values if the cantilever stiffness (i.e. the deflection of the end of the cantilever per unit of applied force), which is usually provided by the manufacturer, is known. The typical stiffness for the cantilevers used in these experiments is specified by the manufacturer as 0.02-0.77N/m. Based on the linear height-deflection relationship obtained in figure 2.5, the deflection signal will change with tip-surface force at a rate of 0.016-0.6V/nN (see caption for figure 2.5). From this, the deflection setpoint values typically used in these experiments (∼1V) translate into an imaging force of 1.7-63nN.

2.3.4 Multi-Channel Image Acquisition

The data collection process is fully automated and software controlled. During the acquisition of a single image, several channels of data can be recorded simultaneously. For the experiments presented here, five data channels were usually recorded. Two channels were used for each of the topography and twist signal images collected during the forward and backward traces of the cantilever, and the last channel was used to monitor the deflection signal (which should remain constant in the ideal case of perfect negative feedback).
Figure 2.5: Plot of AFM deflection signal vs. cantilever height (i.e. the vertical position of the piezoelectric transducer) while the tip is engaged with the surface. Two lines are recorded; one while the cantilever is lowered to the surface, and the other while the cantilever is retracted. The two lines are nearly identical, indicating that the cantilever deforms elastically during the process. The slope of this line along with the manufacturer-specified stiffness of the cantilever allows for a rough force calibration with the deflection signal. For example, the slope of the measured line is roughly -12V/µm. Based on the manufacturer-specified stiffness of 0.02-0.77N/m, a 1µm change in the cantilever height will result in a 20-770nN change in the tip-surface force. This means that a 1nN change in the tip-surface force will result in a change in the deflection signal of 0.016-0.6V (i.e. $12V/770nN = 0.016V/nN$ or $12V/20nN = 0.6V/nN$).
Chapter 3

Grazing-Incidence X-ray Diffraction: Experimental Details

3.1 Experimental Apparatus and Equipment

In the work to be presented in this thesis, Grazing-Incidence X-ray Diffraction (GIXD) is used to obtain detailed information pertaining to the lattice structure, lattice orientation, and single-crystal domain structure of thin tetracene films. This chapter describes the details of the experimental apparatus and procedures that are used in the collection of the data that will be presented in chapter 4. As a convenient reference, a review of the details of diffraction theory that are relevant to this thesis can be found in appendix A.
3.1.1 Synchrotron Facilities

Thin film diffraction experiments will result in a much weaker diffraction signal than diffraction experiments on macroscopic materials. This is because the diffraction process results from scattering of X-rays from electrons within the sample material, and therefore the intensity of the resulting diffraction peaks is directly related to the amount of material present in the sample\(^1\). Because the thin films to be studied are typically only a few molecular layers thick, special steps must be taken to optimize the diffracted intensity in thin film experiments.

To overcome this difficulty, such experiments are usually performed using very intense X-ray beams produced by synchrotron radiation\(^2\) [96]. The brilliance\(^2\) of synchrotron radiation can be over 10 orders of magnitude greater than that of a common laboratory source [97]. This will greatly increase the total rate of scattering events, and hence the diffracted signal, making it possible to conduct experiments that would otherwise be impractical.

The experiments described herein were conducted at two synchrotron facilities. Similar experimental setups were used at each facility. Of the two facilities, the majority of the testing and development of the experimental procedures and techniques was conducted at the Canadian Light Source (CLS) in Saskatoon, Saskatchewan, using the HXMA (Hard X-ray MicroAnalysis) beamline [98].

\(^{1}\)If the sample is a large single-crystal, then all points scatter coherently and the diffracted intensity is proportional to the squared volume of the sample (see equation A.9). However, if the sample contains numerous incoherently-registered crystallites, as is the case in powder diffraction and in the experiments described in this thesis, then the diffracted intensity is directly proportional to the volume of the sample.

\(^{2}\)The brilliance is a quantity often used to characterize the quality of an X-ray source, and is defined as the number of photons emitted per second, per mrad\(^2\) (vertical and horizontal beam divergence), per mm\(^2\) source area, per 0.1\% energy bandwidth. For more discussion, see section 2.2.1 of reference [97].
Most of the data to be presented here was obtained at the second facility, the *Advanced Photon Source* (APS) at Argonne National Laboratory, in Chicago, Illinois, at beamline 20-ID-C. Compared to the CLS, the APS facility offered the advantage of a higher beam brilliance, leading to a shorter data collection time, a smaller beam divergence, and better resolution in the diffraction pattern.

### 3.1.2 The GIXD Apparatus

The GIXD experiment requires the measurement of diffracted intensity at precise positions of the scattering vector $\vec{Q}$, which is defined as the difference between the diffracted and incident beam wavevectors $\vec{k}'$ and $\vec{k}$ respectively. This requires the ability to position the sample and detector in precisely specified orientations with respect to the incident beam. The basic experimental geometry used for achieving this purpose is illustrated in figure 3.1. In the figure, the azimuthal orientation of the sample with respect to the incident beam wavevector $\vec{k}$ is controlled by the angle $\eta$, while the orientation of the detector with respect to the incident beam is given by the angle $\delta$.

The GIXD apparatus is designed to precisely control these orientations. In this section, the major components of the apparatus are described. The main components of the GIXD apparatus are shown schematically in figure 3.2, and a photograph of the apparatus at the APS facility is shown in figure 3.3a.

**Upstream Components**

The upstream portion of the apparatus at the APS facility is shown in figure 3.3b. The X-ray beam enters the experimental hutch through an evacuated beampipe, which
Figure 3.1: The basic geometry of the GIXD experiment. The angles $\eta$ and $\delta$ respectively control the orientations of the sample and detector with respect to the incident beam wavevector $\vec{k}$.
Figure 3.2: Schematic diagram of the main components of the GIXD apparatus. The X-ray beam is directed toward the sample through a pipe which is held under vacuum to minimize attenuation and scattering. The entrance slits are used to shape and size the beam as desired, and the $I_0$ chamber measures the incident beam intensity for normalization of the signal. The components on the detector arm are used to detect the diffracted beam intensity at specified positions. The two detectors are used to measure two different ranges of intensities, while the slits are used to ensure that only a small range of diffracted angles are detected. The filter box is used to attenuate the diffracted intensity when necessary.
minimizes absorption and scattering as much as possible before the beam reaches the sample. After exiting the pipe through a beryllium window, the beam passes through the entrance slits, which shape the beam to the desired dimensions. These slits are remotely controlled, and the slit width is chosen to balance between the need for high intensity, and the need for high-resolution in reciprocal-space, as will be discussed below. The final component before the beam reaches the sample is an ion chamber. This chamber is used to measure the incident intensity of the beam, which is later used for normalization of the measured signal.

The Huber Diffractometer and Sample Chamber

The beam then reaches the sample, which sits at the center of a Huber diffractometer (figures 3.4 and 3.5). The diffractometer controls the precise orientations of the sample and detector by rotating each about several axes, as illustrated in figure 3.4. The sample must be positioned at the rotation center of the diffractometer (i.e. the point where the rotation axes of the diffractometer circles intersect), and its surface must be properly aligned with the incident beam. The procedures for performing these alignments are described in appendix D.

As seen in figure 3.5b, the diffractometer used at the APS is integrated with a vacuum chamber in which the sample is contained during the experiments. While the sample is exposed to the X-ray beam, this chamber is continuously flushed with a stream of helium gas at atmospheric pressure in order to displace air from the chamber. This was intended to prevent the production of ozone by the X-ray beam, which is known to have a detrimental effect on some organic thin-film systems [99,100]. No measurable systematic decay in the resulting diffraction patterns was observed for
Figure 3.3: Some segments of the experimental apparatus at the APS. a) Photograph of the entire apparatus. b) The upstream section through which the beam passes before reaching the sample. c) The downstream section which includes the detectors that measure the diffracted beam.
Figure 3.4: Schematic diagram of the Huber Diffractometer used in the GIXD experiments. Greek letters are used to label the circles, and the arrows indicate their respective directions of rotation. The sample is located at the intersection point of all diffractometer circle rotation axes, with its normal pointing along the $\phi$ axis of rotation. The polarization of the incident beam is horizontal with respect to the laboratory frame, as indicated by the electric field vector $\vec{E}$ in the figure.
Figure 3.5: Photographs of the Huber Diffractometers used for the GIXD experiments at; a) the CLS, and b) the APS. The APS apparatus was integrated with a vacuum chamber. Major components are labelled in each image.
any of the samples, even after several hours of exposure to the X-ray beam.

The vacuum chamber is fitted with two beryllium windows (figure 3.6a). A small beryllium window at the beam entrance position allows the beam to enter the chamber with minimal absorption and scattering, while maintaining the helium environment inside. Similarly, diffracted radiation is allowed to exit the chamber through a large beryllium window on the opposite side from the entrance position. This second window covered a large in-plane angular range to allow the diffracted beam to be detected over a wide range of angles.

**The Detector Arm**

The detector arm of the diffractometer is capable of rotating in any direction about the sample. However for GIXD experiments, since we are mainly interested in the in-plane locations of the crystal truncation rods (discussed in section A.2.1), it is only necessary to deviate a small amount from the plane of the sample surface. The detector arm (figure 3.3c) consists of, in order from upstream to downstream along the diffracted beam trajectory, a set of slits placed in front of an ion chamber (the 1st detector slits), a filter box, and another set of slits placed in front of an Oxford Cyberstar Scintillation Detector [101] (the 2nd detector slits).

The two detectors on the detector arm are each used to measure different magnitudes of diffracted intensities. The Cyberstar detector is a scintillation detector, and is the more sensitive of the two. Therefore it is used for the majority of data-taking. It is also placed further downstream on the detector arm in order to optimize angular resolution. However, since the Cyberstar detector has a limited dynamical range, the ion chamber is used when high intensities are expected.
Figure 3.6: Photographs of the vacuum chamber at the APS in which the sample was contained during the GIXD experiments. a) The beryllium windows through which the beam entered the chamber (top), and the diffracted beam exited (bottom). b) View of the vacuum chamber after opening it, revealing the sample holder inside. This view is facing upstream with respect to the X-ray beam.
The set of slits positioned in front of each detector are used to control the angular resolution during data-collection. A wide slit width will increase the detected intensity, but at the expense of angular resolution.

The filter box contains a set of small aluminum sheets of varying thickness that can be inserted into, or removed from, the beam path by remote control. At times when a high intensity is expected, the filters are used to protect the sensitive Cyberstar detector by reducing the intensity of the beam. This is mainly used during initial detection of the incident beam, and for measuring the profile of the intense substrate diffraction peak.

3.2 GIXD Experimental Procedures

3.2.1 Optimizing the Diffracted Intensity

As mentioned in section 3.1.1, X-ray diffraction on thin films presents the problem that the diffracted intensity will be fairly low owing to the very low amount of material present. This obstacle is mostly overcome by using intense synchrotron radiation, however additional steps should be taken to further optimize the signal. These steps are described in this section.

Setting the Slit Widths

The in-plane (parallel to sample surface) slit widths are an important consideration for optimizing the detected signal. In general, a wider slit setting will increase the amount of detected radiation at the expense of angular resolution. In practice, the slit widths are set as small as possible such that data points may be measured with
a reasonably short integration time. For the experiments that will be presented here, the entrance slits are typically set to 0.4mm along the in-plane direction, while the 2nd detector slits are given an in-plane setting of 0.5mm or 1mm.

On the other hand, the out-of-plane slit widths do not affect the angular resolution in the experiments. This is because we are only interested in the in-plane positions of the crystal truncation rods (discussed in section A.2.1). A wide detector slit width in the out-of-plane direction has the effect of integrating the intensity of the rods in the vertical direction, thus enhancing the signal. For these experiments, the out-of-plane slit width for the 2nd detector slits was set to 10mm. For the entrance slits, an out-of-plane setting of 0.4mm was used for convenience, as this ensured that the beam was wide enough to produce a footprint which spanned the length of the sample.

### Setting the Angle of Incidence of the X-ray Beam

The final, and possibly most crucial optimization parameter is the angle of incidence of the X-ray beam. In section A.2.3, it is shown that a small angle of incidence produces an evanescent wave which travels just below the sample surface, in a direction nearly parallel to the surface. The evanescent wave is diffracted from the crystal structure of the thin film sample, and is thus the source of scattered photons. It must therefore be as intense as possible in order to optimize the diffracted signal.

As shown in section A.2.3, the evanescent wave is at its maximum intensity when the incident angle is at the critical angle for total reflection of the beam. The critical angle is therefore our target when selecting the incident angle.

In order to determine the critical angle, a phosphor screen is placed behind the sample in the incident beam path (figure 3.7a). The phosphor screen glows in areas
where it is exposed to the X-ray beam (figure 3.7b), and thus allows the position of the beam to be observed. A network camera allows the screen to be observed from outside the experimental hutch.

The procedure for determining the critical angle is illustrated in figure 3.7c. We begin with the sample surface held parallel to the incident beam. In this position, the diffractometer circle $\mu$ (see figure 3.4), which directly determines the incident angle, has a value of $0^\circ$. The $\mu$ angle is then incrementally increased, which causes the reflected beam spot on the phosphor screen to diverge from the incident beam spot. Once $\mu$ exceeds the critical angle for total reflection, the reflected beam rapidly disappears. At this point, the critical angle has been found. For our experiments, the critical angle was found roughly to lie in the range of $2.5$-$5$mrad, which is only slightly larger than the value theoretically estimated on page 200 in appendix A.

This procedure is sufficient for enhancing the diffracted intensity enough to detect the diffraction peaks. However, the peak intensities should be optimized further once the peaks are found. This is because the observed disappearance of the reflected beam occurs over several motor steps, and therefore there is a significant amount of uncertainty in the critical angle determination. To further optimize $\mu$, the intensity of the diffraction peak is monitored while $\mu$ is varied in the vicinity of the critical angle. The value of $\mu$ which maximizes the measured intensity is then used for the experimental measurements.

### 3.2.2 Optimizing the In-Plane Resolution in Reciprocal-Space

The goal of the GIXD experiments is to measure the variation in the diffracted intensity with the scattering vector $\vec{Q}$. $\vec{Q}$ is related to the incident and diffracted
Figure 3.7: a) The phosphor screen used to observe the position of the incident and reflected X-ray beam. b) The glowing spots produced on the phosphor screen by the incident and reflected beams, as observed via network camera from outside the experiment hutch. c) Illustration of the procedure used to determine the critical angle. Once the incident angle $\alpha_i$ (which is controlled by the diffractometer circle $\mu$) exceeds the critical angle $\alpha_c$ for total reflection, the incident beam is no longer reflected from the sample surface, and the reflected beam spot disappears from the phosphor screen.
wavevectors, $\vec{k}$ and $\vec{k}'$, which are in turn determined by the diffractometer angles (recall figure 3.4). Therefore, any uncertainties in the diffractometer angles can translate into uncertainties in measured reciprocal-space coordinates.

Figure 3.8 aids in visualizing how the diffractometer angles translate into reciprocal-space coordinates. $\vec{Q}$ is related to the incident and diffracted wavevectors through the equation $\vec{Q} = \vec{k}' - \vec{k}$. The angle $\delta$, which controls the orientation of the detector arm with respect to the incident beam, determines the magnitude of $\vec{Q}$ through the equation:

$$Q = 2k \sin \left( \frac{\delta}{2} \right). \quad (3.1)$$

The angle $\eta$, which controls the azimuthal angle of the sample with respect to the incident beam, will determine the azimuthal orientation of $\vec{Q}$ about the origin in reciprocal-space. As can be determined from the figure, the angle that $\vec{Q}$ makes with the $Q_x$ axis is:

$$\angle \vec{Q} = 90^\circ - \frac{\delta}{2} + \eta. \quad (3.2)$$

More details on mapping diffractometer angles to reciprocal-space coordinates can be found in appendix B.

Clearly, the measurement of diffracted intensity at very precise values of $\vec{Q}$ requires a very precise determination of the incident and diffracted beam orientations with respect to the sample. Ideally, the incident beam will hit the sample at only one precise incident azimuthal angle $\eta$, and the detector will only measure the intensity at one precise exit angle $\delta$. However in reality there will be a finite distribution, or
Figure 3.8: Illustration of how the in-plane diffractometer angles $\delta$ and $\eta$, which control the azimuthal detector and sample orientation respectively, are related to the reciprocal-space point $\vec{Q}$ at which intensity is being measured. The magnitude of the scattering vector $\vec{Q}$ is determined by the angle $\delta$, while the azimuthal orientation of $\vec{Q}$ is controlled by $\eta$. See figure 3.4 for the definitions of the diffractometer angles.
“spread”, of incident and diffracted angles that are detected.

The only source of spread in the incident azimuthal angle $\eta$ is in the divergence of the incident beam (i.e. the distribution of angles that arise due to the incident beam not being perfectly collimated). Due to this divergence, there is a finite distribution of X-ray azimuthal angles $\eta$ that are incident on the sample. In order to minimize the divergence, the experiments are carried out in the vertical scattering geometry, in which the sample surface is held vertical as shown in figures 3.4 and 3.6b. This geometry minimizes the incident beam divergence since the beam divergence in the vertical direction is smaller than that in the horizontal direction (see section 3.7 of reference [96]). We estimate the vertical beam divergence to be on the order of 6$\mu$rad at the APS beamline, and is therefore fairly small (below it will be shown how this value relates to the reciprocal-space resolution).

On the other hand, the magnitude of the angular spread for the diffracted beam is much more significant, and comes from two main effects: The first, shown in figure 3.9a, is the finite-sized “footprint” of the incident beam on the sample surface. Diffracted intensity can potentially come from any point within the footprint, and so a larger footprint leads to a larger range of angles that can be detected. The second effect, shown in figure 3.9b, is due to the finite width of the slits themselves, which will also lead to a finite range of diffraction angles that will be detected.

**Effect of Finite Beam Footprint Size**

The effect of the footprint size can be approximated as follows: Here, the horizontal length of the footprint (i.e. the length measured along the incident beam - see figure 3.9a) is significantly larger than the vertical width (i.e. the footprint width measured
Figure 3.9: The two dominant sources of spread in the angular resolution of $\delta$, the azimuthal exit angle of the diffracted beam. a) A finite beam footprint on the sample will lead to a distribution of exit angles that pass through the set of narrow slits. b) A finite slit width allows X-rays to be detected at a finite-sized range of exit angles. The respective effects have been exaggerated in each diagram for clarity.
transverse to the incident beam), and is therefore assumed to dominate the effect. Referring to figure 3.9a, the horizontal distance $x$ from the slits to the sample, and the vertical distance $y$, are related by $y/x = \tan(\delta)$. We imagine the footprint length $f$ to represent a small variation in $x$, with $y$ held constant. By differentiating this expression, we obtain the relation between the variation in $\delta$ (expressed as $\Delta \delta$) and the footprint length $f$:

$$\Delta \delta_{\text{footprint}} = \frac{y}{x^2} \cos^2(\delta) \cdot f \quad (3.3)$$

Then, after making the substitutions $x = L \cos(\delta)$ and $y = L \sin(\delta)$ (where $L$ is the nominal distance between the sample and slits if the spread is ignored), the angular spread in $\delta$ is related to $f$ by the relation;

$$\Delta \delta_{\text{footprint}} = \frac{f}{L} \sin(\delta). \quad (3.4)$$

For our experimental setup, $L$ is approximately 1m, while the value of $\delta$ for our diffraction peaks is usually around 20°. Since our samples are rectangular, the size of the beam footprint depends on the sample orientation, but will lie approximately within the range defined by the sample width and length (3-10mm). This means that the angular spread in $\delta$, that arises due to the footprint size, will have a full width of about 1-3mrad.

**Effect of Finite Slit Width**

The procedure for estimating the spread due to the finite slit width is somewhat simpler. Referring to figure 3.9b, under the small-angle approximation, the slit gap
subtends an angle of:

\[ \Delta \delta_{slits} = \frac{d}{L}, \]  

(3.5)

where \( d \) is the width of the slit gap, and \( L \), as above, is the slit-sample distance. The same experimental parameters that were used above yield a \( \Delta \delta_{slits} \) value of about 1mrad.

**The Point-Spread-Function (PSF), and the Sampling Window**

From the above calculations, the total spread in \( \delta \) can be estimated as:

\[ \Delta \delta = \sqrt{\Delta \delta^2_{footprint} + \Delta \delta^2_{slits}}. \]

(3.6)

\( \Delta \delta \) will therefore have a value of roughly 1.5-3mrad.

It is important to note that this estimate represents a worst-case scenario. This is because it represents the full range of angles over which the angular distribution is completely contained. It is expected (and shown in section 3.3.2) that the distribution will be approximately Gaussian-shaped, rather than uniform. More weight will therefore be given to angles near the nominal value of \( \delta \), and less weighting to those values near the extremities of the distribution. Therefore the actual angular resolution will tend to be better than this.

The angular distribution discussed above is known as the **point-spread-function** (PSF). The PSF tells us how much “spread” arises in our data due to the limitations of the instrumentation. For example, if a measurement of intensity is being made for a particular value of the azimuthal diffracted beam angle \( \delta \), the PSF tells us the relative
contribution to the total measured intensity of radiation that is being diffracted at some small deviation from \( \delta \).

As a result of the PSF, an intensity measurement at a particular set of \( \eta \) and \( \delta \) values will not result in the sampling of intensity at an exact value of \( \vec{Q} \), but will instead represent the integration of intensity over some finite region of reciprocal-space, referred to here as the *sampling window*, that is centered at \( \vec{Q} \). Measured profiles of diffraction peaks will therefore be artificially broadened due to the finite size of this reciprocal-space sampling window.

### Calculating the Width of the Reciprocal-Space Sampling Window

The relation between the angular width of the PSF and the size of the reciprocal-space sampling window can be derived as follows: The equations used to map diffractometer angles to reciprocal-space coordinates are derived in appendix B, and are given by equation B.26 for the special case of the vertical scattering geometry used in these experiments. By setting \( \phi = 0^\circ \) (note that \( \phi \) performs the same rotation as \( \eta \) in this geometry, and can thus be ignored), the in-plane components of \( \vec{Q} \) given in B.26 can be shown to reduce to:

\[
\vec{Q} = \begin{bmatrix} Q_{xs} \\ Q_{ys} \end{bmatrix} = 2k \sin \left( \frac{\delta}{2} \right) \begin{bmatrix} \sin \left( \frac{\delta}{2} - \eta \right) \\ \cos \left( \frac{\delta}{2} - \eta \right) \end{bmatrix}
\]

The subscript \( S \) signifies that the coordinates are expressed in the sample frame (more details can be found in appendix B).

To find the dimensions of the sampling window, we calculate the magnitude of the change of \( \vec{Q} \) under a small deviation in the angles \( \delta \) and \( \eta \). We call these deviations
\( \Delta \vec{Q}_\delta \) and \( \Delta \vec{Q}_\eta \) respectively. They are calculated as follows:

\[
\Delta Q_\delta = \frac{\partial Q}{\partial \delta} \Delta \delta = k \begin{bmatrix} \sin(\delta - \eta) \\ \cos(\delta - \eta) \end{bmatrix} \Delta \delta
\]

\[
\Delta Q_\eta = \frac{\partial Q}{\partial \eta} \Delta \eta = 2k \sin(\delta/2) \begin{bmatrix} -\cos(\delta/2 - \eta) \\ \sin(\delta/2 - \eta) \end{bmatrix} \Delta \eta
\]

(3.8)

The magnitude of these variations in \( \vec{Q} \) are the effective widths of the sampling window along two directions in reciprocal-space. They can be easily calculated, and are given by:

\[
|\Delta \vec{Q}_\delta| = k \cdot \Delta \delta
\]

\[
|\Delta \vec{Q}_\eta| = 2k \sin \left( \frac{\delta}{2} \right) \cdot \Delta \eta
\]

(3.9)

Note that the vectors \( \Delta \vec{Q}_\delta \) and \( \Delta \vec{Q}_\eta \) are not parallel, and the angle between them can be shown to be \( \frac{\pi}{2} + \frac{\delta}{2} \) using equations 3.8. In our experiments, this angle is roughly 95-102°. Therefore the sampling window is approximately rectangular, and is illustrated in figure 3.10. Note from the figure that the spread in \( \delta \) corresponds to the width of the sampling window in roughly the radial direction, while the spread in \( \eta \) corresponds to the tangential direction.

Using these equations, the size of the sampling window can be estimated using our experimental parameters. The experimental X-ray energy used was 10keV, which corresponds to a wavelength of 1.240\( \text{Å} \), and a \( k \) value of 5.068\( \text{Å}^{-1} \). Again, \( \delta \) is taken to be about 20°. Using the maximum spreads of \( \Delta \eta = 6\mu \text{rad} \) and \( \Delta \delta = 1-3\text{mrad} \) estimated above (see pages 47 and 50 respectively), the radial and tangential widths
Figure 3.10: Visualization of the relation between the spread in the diffractometer angles $\delta$ and $\eta$, and the size of the sampling window in reciprocal-space. The spread in $\delta$ corresponds to the width of the sampling window in roughly the radial direction, while the spread in $\eta$ corresponds to the tangential direction.
of the sampling window are about 5-15×10\(^{-3}\)Å\(^{-1}\) and 10\(^{-5}\)Å\(^{-1}\) respectively. The total area of the reciprocal-space sampling window is therefore about 0.5-1.5×10\(^{-7}\)Å\(^{-2}\).

Note again that these estimates represent the maximum deviations from the nominal \(\vec{Q}\) vector for which intensity is being sampled. The actual PSF gives more weight to small deviations than to large ones, and so the actual reciprocal-space resolution is likely much better than these values would indicate.

**Uncertainty in the Beam Wavevector \(k\)**

It is worth noting that a distribution in the incident beam wavevector \(k\) could theoretically increase the size of the sampling window as well. Therefore the reciprocal-space uncertainty that arises due to uncertainty in \(k\) is analyzed here. According to beamline specifications, the resolution in \(k\) is on the order of \(\Delta k/k \approx 1.4\times10^{-4}\). Using the same approach as above to determine how this uncertainty translates to reciprocal-space, from equation 3.7 we have the following:

\[
\Delta \vec{Q}_k = \frac{\partial \vec{Q}}{\partial k} \Delta k = 2 \sin \left( \frac{\delta}{2} \right) \begin{bmatrix} \sin \left( \frac{\delta}{2} - \eta \right) \\ \cos \left( \frac{\delta}{2} - \eta \right) \end{bmatrix} \Delta k \tag{3.10}
\]

\[
|\Delta \vec{Q}_k| = 2 \sin \left( \frac{\delta}{2} \right) \Delta k \tag{3.11}
\]

With approximate values of \(\delta \approx 20^\circ\) and \(\Delta k \approx 5.07 \times 10^{-4}\)Å\(^{-1}\), the estimated uncertainty in reciprocal-space that arises due to the uncertainty in \(k\) is about 2×10\(^{-4}\)Å\(^{-1}\).

By comparing 3.10 with 3.7, we see that \(\Delta \vec{Q}_k\) is exactly parallel with \(\vec{Q}\), and therefore the spread in \(k\) will lead to a spread along the radial direction in reciprocal-space. This direction is also nearly parallel to \(\Delta \vec{Q}_\delta\) (the angle between \(\Delta \vec{Q}_k\) and \(\Delta \vec{Q}_\delta\) can be shown to be exactly \(\delta/2\), which is approximately 10\(^\circ\) for our experiments).
Therefore the radial spread \((2 \times 10^{-4} \text{Å}^{-1})\) that is due to the uncertainty in \(k\) is small compared to that due to the spread in \(\delta\) \((5-15 \times 10^{-3} \text{Å}^{-1})\) - see page 54. For this reason, the resolution in \(k\) is neglected from the analysis of reciprocal-space resolution.

**Selection of the Incident Beam Energy**

Equations 3.9 suggest that a smaller incident beam energy will improve the radial reciprocal-space resolution. Therefore, the beam energy is chosen to be as small as possible. However, the beam energy may not be set arbitrarily low: There are two important considerations which place lower limits on the beam energy.

The first consideration is the magnitude of the scattering vector \(\vec{Q}\). Equation 3.1 tells us that the magnitude of \(\vec{Q}\) is \(2k\sin(\delta/2)\). Therefore, the magnitude of \(\vec{k}\) must be large enough for \(\vec{Q}\) to reach the reciprocal lattice points that are the subject of the experiment (on the order of \(2 \text{Å}^{-1}\) for these experiments). In order to ensure that diffraction peaks with a \(Q\) value of \(2 \text{Å}^{-1}\) will be diffracted at a convenient angle of 90° or less, equation 3.1 tells us that the incident beam must have a minimum \(k\) value of about \(1.4 \text{Å}^{-1}\), corresponding to a beam energy of 2.76keV.

The second consideration is the absorption energies of the materials through which the beam must pass before reaching the sample and detector. The K-shell absorption edges of many low-Z elements and metals are in the range of a fraction of a keV to a few keV (see section 5 of reference [102]). Resonant absorption occurs for X-rays at these energies, and the absorption cross-section falls off proportional to \(E^{-3}\) \((E\) represents X-ray energy) above the K-edge (see sections 1.3 and 7.1 of reference [97]). Thus unwanted absorption of the X-ray beam will be minimized by selecting a beam energy that is sufficiently higher than the absorption edges of materials that are
expected to be in the beam path.

As a compromise between the considerations discussed here, a beam energy of 10keV was used for the experiments presented in this thesis. However, in future work, it may be worthwhile to experiment with lower energies in order to further enhance the reciprocal-space resolution.

Note that while the beam energy affects the radial resolution $\Delta Q_\delta$ through equation 3.9, it has no effect on the tangential resolution $\Delta Q_\eta$. The factor $2k\sin(\frac{\delta}{2})$ in equation 3.9 reduces simply to $Q$, which is only dependent on the position of the diffraction peak in reciprocal-space, and thus does not vary with beam energy.

### 3.2.3 Data Collection Procedure

After the alignment and optimization procedures, as described in the preceding sections, are complete, the data collection process can begin. Data collection is a two-stage process. In the first stage, the approximate locations of the diffraction peaks are determined and catalogued. In the second stage, two-dimensional high-resolution maps are recorded for some specific peaks of interest. These maps are used to more accurately determine the peak position, and to allow for peak profile analysis.

**Locating the In-Plane Diffraction Peaks**

The strategy for locating diffraction peaks is best understood by visualizing the relation between the diffractometer angles, and the locations of the wavevectors $\vec{k}$ and $\vec{k}'$ in reciprocal-space. As described previously, if the sample is positioned such that the incident beam has wavevector $\vec{k}$, and the detector is positioned so as to detect waves with wavevector $\vec{k}'$, then the position in reciprocal-space for which intensity is being
measured is given by $\vec{Q} = \vec{k}' - \vec{k}$.

As shown in figure 3.11, the above can be visualized by positioning the $\vec{k}$ vector with its tip at the origin of reciprocal-space. The tip of any $\vec{k}'$ vector, when positioned tail-to-tail with $\vec{k}$, must fall on a circular path known as the Ewald Circle, and the corresponding $\vec{Q}$ vector must also fall on the Ewald Circle. If any reciprocal lattice point lies on the Ewald Circle, then a portion of the X-ray beam will be diffracted in the direction corresponding to $\vec{k}'$.

The diffracted beam must be detected via suitable placement of a detector. If available, an Area Detector would provide the most efficient means of peak detection. Such a detector consists of a large, two-dimensional array of X-ray detecting elements, and is therefore capable of sampling a wide angular range with high angular resolution. This means that some large arc-length of the Ewald circle may be observed at once (see figure 3.11). As the sample is rotated (by varying the angle $\eta$), peaks would be observed as they are swept through the Ewald circle, allowing them to be quickly located.

In the experiments presented here, due to the lack of availability of an area detector with sufficient sensitivity, a Point Detector was used (i.e. the Cyberstar scintillation detector). This kind of detector has a single X-ray detecting element, and can therefore only sample a single point on the Ewald circle.

The search for diffraction peaks with a point detector offers a significant challenge in that a two-dimensional region of reciprocal-space with an area of about $2-4\text{Å}^{-2}$ must be searched using a sampling window which spans an area on the order of $10^{-7}\text{Å}^{-2}$ (see page 54). A complete search would therefore take a prohibitively long time, and a less exhaustive searching strategy must therefore be used.
Figure 3.11: Visualization of the diffraction process in reciprocal-space. The Ewald Circle is defined by the circular arc (shown as a dashed line) traced out by the vector $\vec{k}'$ if it is rotated about its tail. If a reciprocal lattice point falls on the Ewald Circle, then X-rays will be diffracted along that particular direction. A point or area detector must be placed along the diffracted beam-path in order to detect the diffracted beam. A point detector is capable of monitoring a small point on the Ewald Circle, while an area detector can monitor a larger segment of the circle. The detector position is determined by the angle $\delta$, and the azimuthal orientation of the Ewald Circle in reciprocal-space is determined by the angle $\eta$. 
In order to initially locate the diffraction peaks, the known positions of the peaks for bulk tetracene is used as a starting point. This is a reasonable first approximation since our previous work has shown that tetracene films take on a bulk-like structure when grown on hydrogen-terminated Si(001) [64], and the crystallized layers are oriented with the a-b plane lying parallel to the sample surface. Therefore, only peaks with indices of the form \((hk0)\) are sought.

**Predicting the Locations of the Tetracene Film Peaks**

The intensities of the various diffraction peaks may be predicted from the unit-cell structure factor, as explained in appendix A. From equation A.9, the intensity of the diffraction peak with index \((hkl)\), which is located at the reciprocal-space position defined by \(\vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\), will be proportional to \(|F(\vec{G})|^2\), which can be calculated using equation A.18.

The detailed structural information needed to carry out this calculation has previously been published by Holmes and co-workers [59], and the lattice parameters are summarized in table 1.1. The peak intensity calculation is shown more explicitly in appendix E. Using this method, the three lowest-order, in-plane diffraction peaks with significant intensities have indices \((1\overline{1})\), \((20)\), and \((2\overline{1})\) (note that, as shown in section A.2.1, for thin films oriented with the a-b plane parallel to the substrate surface, the third index \(l\) is irrelevant, and crystal truncation rods with indices of the form \((hk)\) will be present at the reciprocal-space points given by the in-plane component of the vector \(\vec{G}_{hk} = h\vec{a}^* + k\vec{b}^*\)).

Knowing the indices of these expected intense diffraction peaks, the necessary setting for the angle \(\delta\) may be determined as a starting point in the search for these
peaks. To begin, we must calculate the magnitude of the in-plane component of the reciprocal-lattice vector $\mathbf{G}_{hk}$ corresponding to each peak $(hk)$. To do this, we make use of equation C.5 derived in appendix C, and the known lattice parameters for bulk tetracene as listed in table 1.1. The resulting in-plane magnitudes are as follows:

$$
|\mathbf{G}_{1\parallel}| = 1.360\text{Å}^{-1} \\
|\mathbf{G}_{20\parallel}| = 1.608\text{Å}^{-1} \\
|\mathbf{G}_{21\parallel}| = 1.978\text{Å}^{-1}
$$

Here, the parallel sign $\parallel$ indicates that we have calculated the component of $\mathbf{G}$ that is parallel to the a-b plane.

The relation between $|\mathbf{G}_{hk\parallel}|$ and $\delta$ can be easily derived by simple geometry. From figure 3.11, it can be seen to be

$$
|\mathbf{G}_{hk\parallel}| = 2k \sin \left(\frac{\delta}{2}\right)
$$

Therefore, inserting the experimental $k$ value of $5.068\text{Å}^{-1}$ along with the expected values of $|\mathbf{G}_{hk\parallel}|$ above yields the following values of $\delta$ at which a diffraction peak is expected to be found:

$$
\delta_{1T} = 15.42^\circ \\
\delta_{20} = 18.26^\circ \\
\delta_{2T} = 22.51^\circ
$$
The Peak-Searching Procedure

These values for $\delta$ provide a starting point for the search of the in-plane diffraction peaks with the point detector. With $\delta$ held at these initial values, the $\eta$ circle is rotated while monitoring the intensity. This effectively scans through circles of radius $2k \sin(\delta/2)$ in reciprocal-space.

A peak in the intensity will be recorded whenever a reciprocal lattice vector is swept through the Ewald Circle at a point where the detector lies. An example of the resulting plot will be shown later in figure 4.2. From this plot, the angular positions of diffraction peaks can be easily catalogued.

Measuring Two-Dimensional Reciprocal-Space Maps

Once the diffraction peaks are located, two-dimensional profiles of the diffraction peaks can be measured. This is done by measuring the diffracted intensity for a raster of $\delta$ and $\eta$ points in the vicinity of the detected peaks. From these raster plots, the peak center may be accurately determined, and the intensity profiles can be analyzed.

3.3 Data Processing

3.3.1 Reciprocal-Space Mapping

As has been mentioned in this chapter, most of the analysis to be performed requires the conversion of diffractometer angles to reciprocal-space coordinates. The equations for performing this conversion are fully derived in appendix B. As explained earlier, for the geometry used in the experiments presented here, these equations reduce to
the form given in equation 3.7.

Using equation 3.7, the two-dimensional maps mentioned in section 3.2.3, in which diffraction peak intensity was measured over a raster of $\delta$ and $\eta$ values, may be mapped to a raster of reciprocal-space coordinates. The result is a map of the diffraction peak intensity in reciprocal-space, such as shown in figure 3.12. This technique is used to create the reciprocal-space maps which will be presented in chapter 4.

### 3.3.2 Correcting for Instrumental Peak Broadening (Deconvolution)

**The Point-Spread-Function, and Instrumental Broadening**

In section 3.2.2, the concept of a point-spread-function (PSF) was introduced, which will result in artificial broadening of the measured diffraction peaks. When an intensity measurement is performed at a given value of $\delta$ and $\eta$, the PSF tells us the relative contribution to the measurement from diffracted radiation which has an exit angle of $\delta + \Delta \delta$, and an incident azimuthal angle of $\eta + \Delta \eta$ (i.e. at small deviations from the nominal values of $\delta$ and $\eta$).

We may find a simple relation between the measured signal $y(\delta, \eta)$, the instrumental point-spread-function $psf(\Delta \delta, \Delta \eta)$, and the actual underlying intensity signal $x(\delta, \eta)$ which corresponds to the physical system under study. The measured signal $y(\delta, \eta)$ is effectively a weighted average of the actual signal $x(\delta, \eta)$, where the PSF provides the weighting distribution. Thus the measured signal is simply:

$$y(\delta, \eta) = \int \int psf(\Delta \delta, \Delta \eta) \cdot x(\delta - \Delta \delta, \eta - \Delta \eta) (d\Delta \delta) (d\Delta \eta).$$

(3.15)
Figure 3.12: Example of mapping from diffractometer angles to reciprocal-space coordinates. The plots on the left are 2-D contour plots of intensity measurements as a function of diffractometer angles $\delta$ and $\eta$ for two thin film diffraction peaks. The corresponding plots on the right show the two peaks after the angular coordinates have been mapped to reciprocal-space using equation 3.7.
This is recognizable as the convolution between the PSF and the actual physical signal \( x(\delta, \eta) \):

\[
y(\delta, \eta) = (psf \ast x)(\delta, \eta)
\]  

(3.16)

Clearly this operation has the effect of broadening the measured diffraction peak. Since the PSF originates from the experimental setup, we refer to this effect as instrumental broadening.

As was explained in section 3.2.2, the PSF is much wider along the \( \delta \) direction than along \( \eta \). This means that the instrumentation will tend to artificially broaden the diffraction peaks mostly along the \( \delta \) direction, which corresponds approximately to the radial direction in reciprocal-space.

**Experimental Determination of the Point-Spread-Function**

The two-dimensional reciprocal-space maps of the diffraction peaks may be partially corrected to remove this instrumental broadening. The objective here is to solve equation 3.16 for the actual physical signal \( x(\delta, \eta) \). Such a process is called deconvolution, since it requires solving for one of the operands in the convolution operation.

Obviously from equation 3.16, the deconvolution procedure requires some knowledge of the PSF in order to solve for the actual signal \( x \). It is possible to experimentally determine the shape of the PSF if a peak is available for measurement which is much narrower than the PSF itself. Such a signal could be approximated by a delta
function, in which case equation 3.15 becomes:

$$y(\delta, \eta) = \int \int \text{psf}(\delta', \eta') \cdot \delta(\delta - \delta', \eta - \eta') \, d\delta' \, d\eta'$$

$$= \text{psf}(\delta, \eta).$$  \hspace{1cm} (3.17)

In order to obtain an estimate for the PSF, the silicon substrate (111) peak was used. It is expected that the silicon substrates used in these experiments have single-crystal domain sizes that are very large, and therefore the substrate diffraction peaks will be very narrow (see section 4.3 for a discussion of the relation between domain sizes and peak widths). Therefore, a two-dimensional raster plot of the substrate-peak intensity versus $\delta$ and $\eta$ will approximately result in the instrumental PSF. The result of this measurement is shown in figure 3.13.

Note from the figure that the PSF is significantly wider along the $\delta$ direction than along $\eta$, as expected. The full width of the distribution along the $\delta$ and $\eta$ directions are roughly $0.08^\circ$ and $0.015^\circ$ respectively. Using equations 3.9, these translate to radial ($\Delta Q_\delta$) and tangential ($\Delta Q_\eta$) resolutions of about $7 \times 10^{-3} \text{Å}^{-1}$ and $4.6 \times 10^{-4} \text{Å}^{-1}$ respectively. The value for $\Delta Q_\delta$ compares well with the theoretical range (5-15$ \times 10^{-3} \text{Å}^{-1}$) given on page 54, but the value for $\Delta Q_\eta$ is about a factor of ten larger than its respective theoretical value ($10^{-5} \text{Å}^{-1}$). The disagreement in $\Delta Q_\eta$ is an indication that, either the incident beam collimation is not as good as we have estimated (which would result in a broader PSF along $\eta$), or that the substrate peak is not narrow enough to be approximated as a delta function (in which case the substrate peak measurement does not exactly represent the PSF). In either case, the measurement shown here serves sufficiently well as an approximation of the PSF.
Figure 3.13: Reciprocal-space map of the silicon substrate (111) peak which was used as an estimate for the point-spread function. The plot was recorded with a detector slit width of 1 mrad. The plot shows that there is significantly more spread along the $\delta$ direction than along the $\eta$ direction. (The origin of the secondary peak at the lower-right corner of the plot is uncertain, but is believed to be a result of refraction from a tungsten clip that was used during this measurement.)
The Deconvolution Algorithm: Wiener Filtering

There are several approaches to the problem of deconvolution [103, 104] (also known as “inverse filtering”), and a few were tested for the data presented in this thesis. Here, the algorithm which yielded the best results is described.

In order to simplify the process, the broadening of the peaks along the $\eta$ direction is ignored. As argued previously, broadening in the $\eta$ direction is significantly less than in the $\delta$ direction. Therefore, for computational convenience, the deconvolution algorithm aims to remove broadening along the $\delta$ direction only. A one-dimensional deconvolution procedure is thus applied to the rows of intensity versus $\delta$ data that form the images.

It is also important to note that the functions of interest are discrete series of digital measurements. Therefore, for the purposes of this discussion, we will represent the functions of interest as discrete functions of index $n$ (where each value of $n$ corresponds to a value of $\delta$). For example, $y[n]$ represents the $n^{th}$ value of the series of experimentally obtained intensity measurements.

The objective is to obtain an estimate for the actual physical signal $x[n]$. To do this, a Wiener filter [103–105] is applied to the measured signal. In this approach, the measured signal $y[n]$ is assumed to have the form;

$$y[n] = psf[n] * x[n] + v[n]$$

where the extra term $v[n]$ represents random noise in the measurement. The Wiener filter $g[n]$ is a function that, when convolved with $y[n]$, yields an estimate $\hat{x}[n]$ for $x[n]$ in which the mean-square error between $x$ and $\hat{x}$ (which arises due to random
noise) is minimized. The form of the filter in Fourier space which satisfies this objective is:

\[ G[k] = \frac{PSF^*[k] \cdot |X[k]|^2}{|PSF[k]|^2 \cdot |X[k]|^2 + < |V[k]|^2 >}. \]  \hspace{1cm} (3.19)

Here, capital letters are used to represent the Discrete Fourier Transform of each respective function, the superscript asterisk (*) represents complex conjugation, and \(< |V[k]|^2 >\) is the mean-square value of the random noise term.

The benefit of this approach is that it is computationally convenient, and allows random electronic noise to be corrected for. Examples of raw and deconvolved diffraction peaks are shown in figure 3.14a and b.

The noise term \(< |V[k]|^2 >\) is a free parameter of the filter. For the procedure used here, the noise was simply taken to be a small fraction of the maximum intensity for a peak (typically on the order of one hundredth). It is easy to tell if the noise estimate is too high, as the peak becomes broad and rounded as compared to the raw peak (see figure 3.14c for an example).

Note also that the Wiener filter in equation 3.19 requires, as a parameter, the expected Fourier spectrum of the solution signal \(|X[k]|^2\). To serve this purpose, an estimate of the solution \(x[n]\) suffices. (This is especially true if the noise term \(|V[k]|^2\) is small, as this will render the solution spectrum factor \(|X[k]|^2\) unimportant, as can be seen from equation 3.19.). Therefore the Discrete Fourier Transform of the measured signal \(y[n]\) is used as a guess at \(X[k]\) in the application of the filter.

A sample of the code used to apply the Wiener filter can be found in appendix F. The algorithm can be summarized as follows:
Figure 3.14: Examples of applying the deconvolution procedure to the data. Note that these figures are plotted in reciprocal-space coordinates, even though the data processing is carried out in angular coordinates. All images are shown to the same scale. Black arrows indicate the direction of increasing $\delta$ (i.e., the direction of instrumental broadening, also referred to as the radial direction). a) Raw data peaks. b) The processed peaks after Wiener filtering. Note that the processed peaks have narrowed along the radial direction. c) Example of a filtered peak in which the noise parameter was set too high (in this case, the noise amplitude has been set roughly equal to the maximum intensity of the raw peak). Notice that the peaks have been slightly broadened along the radial direction with respect to the raw peak. d) Example of a filtered peak in which the PSF width was set too large. Notice that oscillations appear along the radial direction.

2. Construct the Wiener Filter in Fourier space, $G[k]$, using equation 3.19. In this equation, the Fourier Transform of the measured signal $Y[k]$ found in step 1 is used as the estimate $X'[k]$ of the physical signal in Fourier space.

3. In Fourier space, multiply the Wiener Filter $G[k]$ by the measured signal $Y[k]$ to obtain the final estimate for the true physical signal $\hat{X}[k]$.

4. The inverse Fourier Transform of $\hat{X}[k]$ will be the final estimate of the deconvolved signal $\hat{x}[n]$.

**Setting the PSF Width in the Deconvolution Algorithm**

As discussed in section 3.2.2, the PSF width will change with sample orientation and peak position since the beam footprint size on the sample varies with sample orientation. Since the substrate peak is only measured at one particular sample orientation, the measured PSF can not be applied to all of the diffraction peaks. Instead, the width of the PSF is varied for each peak. Therefore the PSF width is used as a variable parameter in the deconvolution procedure described above.

The criterion for setting the PSF width was the onset of oscillations in the estimate $\hat{x}[n]$ of the physical diffraction peak $x$. The oscillations occur if the assumed width of the PSF is too large (for example, see figure 3.14d).
Effectiveness of the Deconvolution Procedure

In the end, the benefit of the deconvolution procedure is twofold: It allows for improvements in the cosmetic appearance of the diffraction peaks (as shown in figure 3.14), allowing for more convincing evidence that the peaks are actually elongated in particular directions (this is an important result for the discussion in chapter 4), and it allows for an estimation to be made of the experimental error that is introduced as a result of instrumental broadening. The estimated errors given in chapter 4 reflect the differences in the peak widths measured before deconvolution, and after deconvolution using the maximum PSF width (i.e. at the onset of oscillations, as described above).
Chapter 4

Characterization of the Film Structure by GIXD

Grazing-incidence X-ray diffraction (GIXD) may be used to obtain rich information regarding the structure of crystalline thin-films. The focus of this chapter is to present the results of GIXD experiments in which these concepts are applied to tetracene films grown on the Si(001)-monohydride surface. The GIXD results are first presented and used to characterize the lattice structure, and to determine preferred lattice orientations. The intensity profiles of film diffraction peaks are then analyzed in order to determine the preferred growth direction of the single-crystal domains which comprise the films, and to estimate their size. Lastly, GIXD is used to study tetracene films on high step-density substrates in order to see the effects of substrate steps on the single-crystal domains.
4.1 Sample Preparation

In order to produce results that could be compared to, and extend those of our previous experiments, the same sample preparation apparatus and procedure were used [64, 65, 73, 106]. Sample preparation was carried out in a two-chamber ultra-high vacuum (UHV) system. The silicon(001)-monohydride substrate was prepared by annealing the silicon wafer at least two times at \( \sim 1470 \) K for about 1min in the first chamber (base pressure of \( \sim 1 \times 10^{-10} \) torr), and then using a hot tungsten filament (\( \sim 1800 \) K) to generate atomic hydrogen while back-filling the chamber with molecular hydrogen (\( \sim 10^{-6} \) torr) for 20 min to form a silicon-monohydride \( 2 \times 1 \) surface at \( \sim 600 \) K. Two types of silicon substrates were used, with miscut angles of 0.03° and 0.3° toward the [110] direction (i.e., the surface normal deviates from the lattice [001] direction, and tilts towards the [110] direction by these angular amounts) and hence terrace widths (or substrate-step spacings) of \( \sim 2600 \) Å and \( \sim 260 \) Å, respectively. Monolayers (ML) of tetracene films were grown in the second chamber (base pressure of \( \sim 3 \times 10^{-9} \) torr) by thermal evaporation of tetracene from an alumina crucible heated by a tungsten basket, at a deposition rate of 0.8ML/min. A quartz crystal microbalance (QCM) was used to monitor the deposition rate which was controlled by adjusting the temperature of the crucible. The QCM reading had previously been calibrated by atomic-force microscopy (AFM) imaging. The tetracene films described here are 1.5, 4, and 12ML in thickness.
4.2 Lattice Structure and Lattice Orientation

4.2.1 Determination of the Film Lattice Orientation by GIXD

In our previous work (sumarized in section 1.5), it was shown that tetracene films grown on the silicon(001)-monohydride surface form a bulk-like structure in which the molecules stand upright on the surface, with the $\vec{a}$ and $\vec{b}$ vectors (i.e. the a-b plane - see figure 1.2) lying parallel to the sample surface. AFM topographs, such as that in figure 4.1, reveal a layered film morphology. The upper-layer islands are elongated, with dendritic branches extending at 90° angles from the long axis. The long axes of the islands are aligned dominantly along two orthogonal directions, the substrate (110) or (110) directions.

This upright orientation of the tetracene molecules in the thin films can be understood simply in terms of surface energetics. Theoretical calculations for pentacene (another polyacene consisting of five fused benzene rings) show that the (001) surface is lowest in surface energy [63]. Therefore, there is a thermodynamic preference for the film lattice to be oriented with this face upwards in order to minimize the overall energy of exposed surfaces. Given the similarities in structure between tetracene and pentacene, this argument likely applies to the tetracene films as well.

This provides a starting point in our search for diffraction peaks in the GIXD experiments. Since the tetracene lattice is oriented with the (001) direction normal to the substrate surface, only diffraction peaks corresponding to the tetracene a-b plane are sought (i.e. diffraction peaks with indices of the form $(hk0)$). The lowest-order, in-plane diffraction peaks with the highest expected intensities have indices (110), (200), and (210) (see appendix E).
Figure 4.1: Large-scale AFM topograph of a 4ML tetracene film grown on an atomically flat Si(001)-monohydride surface. The black arrows indicate the two dominant orientations of the island long-axes. The substrate (110) and (1T0) directions are also indicated.
The procedure for locating the in-plane diffraction peaks is outlined in detail in section 3.2.3. The $\delta$ circle (see figures 3.4 and 3.8) is held at an angle at which a bulk peak is expected, and the $\eta$ circle is rotated while the diffracted intensity is monitored. By this method, the diffracted intensity is measured along circular arcs in reciprocal-space, producing line-scans such as that shown in figure 4.2.

**Discrete versus Continuous Lattice Orientations**

The line-scans of figure 4.2 clearly show a set of discrete diffraction peaks. This demonstrates that only certain lattice orientations are able to exist within the film. In contrast, for a film consisting of a continuous distribution of lattice orientations, each diffraction peak would effectively exist at all possible azimuthal orientations about the origin, and the resulting diffraction pattern would consist of concentric rings centered at the origin.

Such a diffraction pattern consisting of concentric rings was, in fact, observed for tetracene films grown on hydrogen-terminated silicon(001) which was prepared by hydrofluoric acid (HF) etching [107]. The HF-etched substrate is much rougher than those prepared in the vacuum chamber by the method described in section 1.4 [108], and therefore has a more isotropic surface. This demonstrates that the effect of the well-ordered, periodic structure of the Si(001)-monohydride surface is to confine the film lattice to specific orientations.

**Identification of the Preferred Lattice Orientations**

The GIXD data show that there are dominantly two sets of discrete in-plane Bragg peaks existent for the films, suggesting that two orthogonal but otherwise identical
Figure 4.2: A sample of the data collected during the peak-searching process. Each plot was recorded by rotating the $\eta$ circle while holding the $\delta$ circle fixed at a position for which a bulk peak is expected (see section 3.2.3). The index of the peaks corresponding to each line scan are indicated in the legend. Using this method, the most intense peaks are easily located. The observation of diffraction peaks in discrete positions indicates that only particular lattice orientations are present in the film, as opposed to a continuous distribution of lattice orientations. Note that for the purposes of clarity, the intensity scales of the $(1\bar{1})$, $(20)$ and $(2\bar{1})$ scans have been enlarged in a scale of 1:1, 4:1 and 1.4:1 respectively. Note also that the regions marked “dead zone” are regions of reduced intensity that result from blockage of the incident or diffracted beam by non-removable pieces of the sample holder (shown in figure 3.6b), which protrude above the sample surface.
lattice orientations or domains are dominant in the coalesced tetracene monolayers. Figure 4.3a presents a reciprocal-space map of GIXD peaks detected for a 4ML tetracene film grown on a 0.03°-miscut substrate. Black dots represent the locations where the in-plane diffraction peaks are found, and some two-dimensional contour plots of selected peaks are overlaid on their respective coordinates. As described above, the positions of these peaks correspond to the approximate expected positions of the bulk (1\bar{1}), (2\bar{1}), and (20) peaks, and are indexed as such in the figure. Evidently, there are two types of unit-cell orientations that are perpendicular to each other, as illustrated by red and green dashed lines. All of the detected peaks of significant intensity match one of these two orientations. In order to determine the film lattice orientation relative to the substrate, the position of the silicon(111) peak was measured, and its projected position on the a-b plane is indicated by a blue star in the figure. Based on this peak position, the two tetracene lattice orientations are such that the $\vec{b}$ direction of the tetracene film is aligned either parallel or perpendicular to the (110) direction of the substrate lattice.

In order to assist in visualizing the relationship between the film and substrate lattice orientations, figure 4.4 depicts the tetracene lattice on the silicon(001) surface in the orientations that were determined from the GIXD data (Note that while the figure presents an overlay of the tetracene lattice on the silicon surface, the actual position at which the tetracene lattice is registered on the surface is unknown from these experiments, and the figure is used to illustrate the relative orientations only.). The rows of tetracene molecules are aligned parallel or perpendicular to the rows of silicon dimers on the substrate surface. As shown in the figure, the silicon substrate surface consists of alternating terraces separated by atomic steps. On adjacent ter-
Figure 4.3: a) Two-dimensional reciprocal-space map of measured diffraction peaks for a 4ML tetracene film grown on a 0.03°-miscut Si(001)-monohydride surface. The red and green dashed lines indicate the two sets of reciprocal-space unit cells with the corresponding molecular lattices shown, and the projections of the reciprocal-lattice vectors $\mathbf{a}^*$ and $\mathbf{b}^*$ onto the a-b plane are indicated. The indices of the peaks indicate the most significant in-plane diffraction peaks, given the coexistence of domains with either $\mathbf{a}^*$ or $\mathbf{b}$ rotated 180° (see text for more discussion). Substrate lattice coordinates are indicated on the left side, and the projected position of the bulk silicon (111) peak is indicated with a blue star. The positions of all detected GIXD peaks of significant intensity are indicated by black dots. Contour plots of selected peaks are enlarged in a scale of 30 : 1 and overlaid on the respective coordinates. b) Line profiles showing cross sections of the numbered peak; each curve is a least-squares fit to the raw data. $\Delta q$ indicates a relative position in reciprocal-space. The typical resolution shown is the average of the radial and transverse resolutions (see sections 3.2.2 and 3.3.2).
races, the dimer rows are aligned along orthogonal directions, as explained in section 1.3. These two terrace orientations are likely responsible for the two film orientations which were identified above.

Existence of Additional, 180°-Rotated Lattice Orientations

Note that while the structure factor calculations predict that the (11) and the (21) peaks should be insignificant in intensity as compared with the (11) and (21) peaks respectively (see table E.1 in appendix E), we still detected peaks with significant intensity at these positions. For instance, in surveying line scans such as that shown in figure 4.2, it was found that the nominal (11) in-plane peak in figure 4.3a (the unmapped black spot at the end of the red $\vec{b}$ vector) has a similar peak intensity as that of the mapped (11) peak, with a difference of less than 1%. On the other hand, according to the estimated structure factor using the bulk tetracene lattice parameters, the expected (11) peak intensity should be only $\sim 6\%$ of that of the (11) peak. This indicates that there exist a significant number of domains in the film with their $\vec{a}^*$ axis direction inverted 180° from the $\vec{a}^*$ direction shown in figure 4.3a. Similar observations hold true for the mapped peak at the nominal (21) position (indexed as the (21) peak for the red domains in figure 4.3a), which would be insignificant (two orders of magnitude weaker) according to the structure factor estimation. Therefore, for each of the two apparent domain orientations that we detect, there could be three others associated with it, each representing a domain after rotation of 180° about the $\vec{a}$, $\vec{b}$, or $\vec{c}^*$ axes (note: $\vec{c}^*$ is parallel to the surface normal). These additional domains would have the same in-plane lattice constants, and would thus be indistinguishable in the in-plane diffraction data. In other words, for the red and green domains
Figure 4.4: Illustration of the two possible film-substrate registrations that were detected in the GIXD data. Both orientations of the Si(001) terraces which exist on the substrate surface are shown. Note that while the figure presents an overlay of the tetracene lattice on the silicon surface, the actual position at which the tetracene lattice is registered on the surface is unknown from these experiments, and the figure is used to illustrate the relative orientations only.
shown in figure 4.3a, there exist equivalent domains with \( \vec{a}^* \) or \( \vec{b}^* \) pointing in opposite directions, respectively. In indexing of the in-plane diffraction peaks in figure 4.3a, we marked only the indices which are the most significant in intensity according to the estimation based on calculated structure factors (e.g., the marked (21) peak in figure 4.3a is in fact at the position of peak (21) for the particular \( \vec{a}^* \) and \( \vec{b}^* \) orientations shown in the figure.).

The existence of these additional lattice orientations will have significance in section 5.2.2, where the LFM results are interpreted and discussed.

4.2.2 The In-Plane Lattice Parameters, and Partial Commensurability with the Substrate

The fact that the two domains follow the orientations of the substrate lattice is in good agreement with our previous STM study [64], in which real-space images showed that the tetracene film lattice is commensurate with the silicon substrate along the film \( \bar{a} \) axis, suggesting a non-negligible influence of the substrate lattice in the film nucleation and growth.

The observation of a partially epitaxial relationship is further supported by measurement of the in-plane lattice parameters, as determined from the diffraction peak positions in the GIXD data. The parameters are determined by least-squares fitting of calculated peak positions to the experimentally measured peaks. The results for tetracene on the Si(001)-monohydride surface are summarized in table 4.1 (for convenient comparison in the discussion below, the table also lists the lattice parameters for bulk tetracene, and for tetracene films grown on the isotropic HF-etched substrate mentioned on page 76). For the Si(001)-monohydride surface, the measure-
Table 4.1: Comparison of lattice parameters for the thin-film phase of tetracene with that of the bulk structure. The bulk values are as reported by Holmes and co-workers [59]. The thin film parameters are given for two substrates: the well-ordered, periodic Si(001) monohydride surface; and the disordered HF-etched Si(001) substrate. The thin film parameters were measured for film thicknesses of 1.5ML, 4ML, and 12ML, and were found to agree within uncertainty for all three thicknesses.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk structure</td>
<td>7.8376Å</td>
<td>6.0565Å</td>
<td>85.79°</td>
</tr>
<tr>
<td>thin film on Si(001)-monohydride</td>
<td>7.70±0.02Å</td>
<td>5.93±0.02Å</td>
<td>90.0°±0.2°</td>
</tr>
<tr>
<td>thin film on HF-etched Si(001)</td>
<td>7.64±0.02Å</td>
<td>5.91±0.02Å</td>
<td>89.9°±0.3°</td>
</tr>
</tbody>
</table>

The measurements shown in table 4.1 indicate a slight compression (as compared with the bulk value) of the tetracene lattice along the $\vec{a}$ direction to match, within the estimated uncertainty, the substrate periodicity of 7.68Å, verifying the partially-commensurate film-substrate relationship mentioned above. This shows that the effect of the well-ordered Si(001)-monohydride surface is to lock the substrate into a strained structure in order to match its own periodicity. However this commensurability does not apparently apply to the $\vec{b}$ direction since the $b$ parameter does not match the periodicity of the silicon substrate (There is a possibility that commensurability exists over many unit cells, however this would not be detectable with the present data.).

It is interesting to note from table 4.1 that, for films grown on the disordered, HF-etched Si(001) substrate, the lattice parameter ‘$a$’ is slightly smaller than for films grown on the well-ordered Si(001)-monohydride surface [107]. Since the HF-etched substrate is amorphous and isotropic, this indicates that the well-ordered, periodic structure of the monohydride surface is not necessarily responsible for the compression. Instead, it is possible that tetracene films naturally take on a “thin-film phase” that is different from the bulk structure. The existence of thin-film
structures which are different from the bulk structure has previously been observed in tetracene [109] and pentacene [110,111] films. In this case, the well-ordered Si(001)-monohydride surface may actually be responsible for a slight in-plane expansion of the film along the \( \vec{a} \) direction as compared with films grown on the disordered HF-etched substrate.

### 4.3 Diffraction-Peak Profile Analysis

In this section, the mathematical basis for the diffraction-peak intensity-profile analysis is presented. The concepts developed here will be used in section 4.4 to estimate the sizes and shapes of the single-crystal domains that make up the tetracene films. However, a complete understanding of the derivations contained here is not necessary to understand the experimental results presented later, and therefore this section may be skipped, depending on the interest of the reader.

First, it is shown how to calculate the diffracted intensity profile in reciprocal-space for a two or three-dimensional crystallite. It is then shown how the measured intensity profile may be used to estimate the size of a crystallite. Finally, the effect of coherent or incoherent registration of multiple crystallites on the total diffracted intensity profile is discussed.

#### 4.3.1 Diffraction-Peak Intensity Profile for a Single Crystallite

We first find the relation between the intensity profile of a diffraction peak, and the shape of the crystallite. The discussion presented here is adapted for the purpose
of the analysis presented in this thesis. For a more thorough discussion of X-ray diffraction intensity in general, see Als-Nielsen and McMorrow [97].

**Diffracted Intensity in the Vicinity of a Reciprocal Lattice Point**

As shown in section A.1.2, the diffracted amplitude from a crystallite can be written as the sum of diffracted amplitudes from all unit cells within the crystal. We therefore use equation A.4 as a starting point, which states that the diffracted amplitude $S$ can be expressed as follows:

$$
S(\mathbf{Q}) \propto F(\mathbf{Q}) \sum_{n_a, n_b, n_c} e^{-i\mathbf{Q} \cdot (n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c})}
$$

(4.1)

Here, $\mathbf{Q}$ is the scattering vector, defined in terms of the incident and diffracted wavevectors ($\mathbf{k}$ and $\mathbf{k}'$ respectively) as $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$; $F(\mathbf{Q})$ is the structure factor of a single unit cell (defined by equation A.18); the vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are the primitive lattice vectors; and the integers $n_a$, $n_b$, and $n_c$ are used to index the positions of each unit cell respectively along the $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ directions. The sum is taken over all values of $n_a$, $n_b$, and $n_c$ for which a unit cell can be found at the position $\mathbf{R}_n = n_a \cdot \mathbf{a} + n_b \cdot \mathbf{b} + n_c \cdot \mathbf{c}$, and therefore the expression is intrinsically related to the shape and size of the crystal.

We are interested in the profile of the scattering amplitude in the vicinity of a diffraction peak, which will be centered at the position of a reciprocal lattice vector $\mathbf{G}$. We therefore write the scattering vector as $\mathbf{Q} = \mathbf{G} + \mathbf{q}$, where $\mathbf{q}$ represents a small deviation from the reciprocal lattice vector $\mathbf{G}$. Equation 4.1 can then be re-written
as;

\[ S(\vec{Q}) \propto F(\vec{Q}) \sum_{n_a, n_b, n_c} e^{-i(\vec{G}+\vec{q}) \cdot (n_a \vec{a} + n_b \vec{b} + n_c \vec{c})}. \] (4.2)

Since by definition, the dot product of a reciprocal lattice vector $\vec{G}$ with a real-space lattice vector $\vec{R}_n = n_a \vec{a} + n_b \vec{b} + n_c \vec{c}$ is $2\pi$ times an integer, we obtain the simplified expression;

\[ S(\vec{Q}) \propto F(\vec{Q}) \sum_{n_a, n_b, n_c} e^{-i\vec{q} \cdot (n_a \vec{a} + n_b \vec{b} + n_c \vec{c})}. \] (4.3)

We now have an expression for the amplitude in terms of some small deviation $\vec{q}$ from a reciprocal lattice vector. It is computationally convenient to approximate this sum as an integral over the indices $n_1, n_2,$ and $n_3$:

\[ S(\vec{Q}) \propto F(\vec{Q}) \int \int \int dn_1 dn_2 dn_3 e^{-i\vec{q} \cdot (n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c})} \] (4.4)

The approximation is valid if the integrand changes slowly with the indices. The conditions under which this is true will be examined below.

We now perform a change of variables so that we can integrate over spatial variables $x, y,$ and $z,$ instead of the unit cell indices $n_1, n_2,$ and $n_3$. The following
substitutions are made:

\[ x = n_1 a_x + n_2 b_x + n_3 c_x \]
\[ y = n_1 a_y + n_2 b_y + n_3 c_y \]
\[ z = n_1 a_z + n_2 b_z + n_3 c_z \]  \hspace{1cm} (4.5)

After the change of variables, the scattering amplitude is expressed as

\[
S(\vec{Q}) \propto F(\vec{Q}) \int\int\int_{V_{\text{crystal}}} dx
dy
dz \frac{V_{\text{cell}}}{e^{-i\vec{q} \cdot \vec{r}}},
\]

where \( \vec{r} \) is the position vector, and \( V_{\text{cell}} \) is the volume of a unit cell. The integral is taken over the entire volume of the crystal, and is recognizable as the Fourier Transform of the crystal shape.

Finally, the scattered intensity \( I(\vec{Q}) \) can be expressed in its final form as

\[
I(\vec{Q}) \propto |S(\vec{Q})|^2 \propto \left| \frac{F(\vec{Q})}{V_{\text{cell}}} \int\int\int_{V_{\text{crystal}}} dV e^{-i\vec{q} \cdot \vec{r}} \right|^2.
\]  \hspace{1cm} (4.7)

Validity of the Approximation

We now examine the conditions under which the approximation of the sum in 4.3 to the integral in 4.4 is valid. The approximation is valid if the integrand changes slowly with each of the variables of integration, or equivalently;

\[
e^{i\vec{q} \cdot (n_1+1)\vec{a}+n_2\vec{b}+n_3\vec{c})} \approx e^{i\vec{q} \cdot (n_1\vec{a}+(n_2+1)\vec{b}+n_3\vec{c})} \approx e^{i\vec{q} \cdot (n_1\vec{a}+n_2\vec{b}+(n_3+1)\vec{c})} \approx e^{i\vec{q} \cdot (n_1\vec{a}+n_2\vec{b}+n_3\vec{c})}.
\]  \hspace{1cm} (4.8)
Simplifying, we have;

\[ e^{i\vec{q} \cdot \vec{a}} \approx e^{i\vec{q} \cdot \vec{b}} \approx e^{i\vec{q} \cdot \vec{c}} \approx 1, \quad (4.9) \]

or;

\[ |\vec{q} \cdot \vec{a}|, |\vec{q} \cdot \vec{b}|, |\vec{q} \cdot \vec{c}| \ll \frac{\pi}{2}, \quad (4.10) \]

which will be true for all values of \( q = |\vec{q}| \) where

\[ q \ll \frac{\pi}{2a}, q \ll \frac{\pi}{2b}, q \ll \frac{\pi}{2c}. \quad (4.11) \]

Equation 4.11 tells us that the approximation in 4.4 is valid for sufficiently small values of \( q = |\vec{q}| \). That is, equation 4.4 (and therefore equation 4.7) is valid if \( \vec{Q} \) is sufficiently close to a reciprocal lattice vector \( \vec{G} \). Therefore if the integral in equation 4.7 decays to zero long before the condition in 4.11 is violated, then the approximation of equation 4.4 is valid everywhere. We will now examine the conditions under which this is the case.

As a simple example, consider a crystal in the shape of a parallelepiped, whose axes extend along the crystallographic directions \( \vec{a}, \vec{b}, \) and \( \vec{c} \), as shown in figure 4.5. Let \( N_a, N_b, \) and \( N_c \) represent the number of unit cells that the crystal contains in each of these directions, respectively, and let one vertex be situated at the origin. Starting from equation 4.4, we express \( \vec{q} \) as a sum of reciprocal lattice basis vectors \((\vec{q} = q_a^* \vec{a}^* + q_b^* \vec{b}^* + q_c^* \vec{c}^*)\) and write

\[ S(\vec{Q}) \propto F(\vec{Q}) \int \int \int dn_1 dn_2 dn_3 e^{-i(q_a^* \vec{a}^* + q_b^* \vec{b}^* + q_c^* \vec{c}^*) \cdot (n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c})}, \quad (4.12) \]

where \( q_a^*, q_b^*, \) and \( q_c^* \) are the components of \( \vec{q} \) in the directions of \( \vec{a}^*, \vec{b}^*, \) and \( \vec{c}^* \).
Figure 4.5: A parallelepiped-shaped crystal with its axes oriented parallel to the $\hat{a}$, $\hat{b}$, and $\hat{c}$ directions.
respectively. Using the definition of the reciprocal lattice basis vectors, this can be simplified as

\[
S(\vec{Q}) \propto F(\vec{Q}) \int \int \int d{n_1} \, d{n_2} \, d{n_3} \cdot e^{-i\frac{2\pi}{a}n_1q_a} e^{-i\frac{2\pi}{b}n_2q_b} e^{-i\frac{2\pi}{c}n_3q_c}
\]

\[
\propto F(\vec{Q}) \int_{0}^{N_a} d{n_1} e^{-id_a n_1q_a} \int_{0}^{N_b} d{n_2} e^{-id_b n_2q_b} \int_{0}^{N_c} d{n_3} e^{-id_c n_3q_c}
\]

\[
\propto F(\vec{Q}) \frac{1}{-id_a q_a} (e^{-id_a N_a q_a} - 1) \frac{1}{-id_b q_b} (e^{-id_b N_b q_b} - 1) \frac{1}{-id_c q_c} (e^{id_c N_c q_c} - 1). \tag{4.13}
\]

Here, \(d_a = 2\pi/a^*\), \(d_b = 2\pi/b^*\), and \(d_c = 2\pi/c^*\) are the distances between lattice planes in the \(a^*\), \(b^*\), and \(c^*\) directions respectively. After more simplification, the intensity can finally be expressed as

\[
I(\vec{Q}) \propto |S(\vec{Q})|^2 \propto |F(\vec{Q})|^2 \left( \frac{2 - 2\cos(d_a N_a q_a)}{d_a^2 q_a^2} \right) \left( \frac{2 - 2\cos(d_b N_b q_b)}{d_b^2 q_b^2} \right) \left( \frac{2 - 2\cos(d_c N_c q_c)}{d_c^2 q_c^2} \right)
\]

\[
\propto |F(\vec{Q})|^2 \left( \frac{\sin(d_a N_a q_{a/2})}{d_a q_a/2} \right)^2 \left( \frac{\sin(d_b N_b q_{b/2})}{d_b q_b/2} \right)^2 \left( \frac{\sin(d_c N_c q_{c/2})}{d_c q_c/2} \right)^2 \tag{4.14}
\]

The bracketed factors have a maximum value (at \(q=0\)) of \(N_a^2\), \(N_b^2\), and \(N_c^2\) respectively, have their first zero at \(dNq = \pi\), and oscillate thereafter with diminishing amplitude. Again, the objective is to determine the conditions on the crystal that will have the scattered intensity decay to zero long before \(q\) reaches the upper limits in equation 4.11. If we loosely take the first zero of each \(q\) component as the upper limit at which any significant intensity can be measured, then condition 4.11 will be satisfied if

\[
\frac{\pi}{d_a N_a} \ll \frac{\pi}{2a}, \quad \frac{\pi}{d_b N_b} \ll \frac{\pi}{2b}, \quad \frac{\pi}{d_c N_c} \ll \frac{\pi}{2c}. \tag{4.15}
\]
or;

\[ d_a N_a \gg 2a \ , \ d_b N_b \gg 2b \ , \ d_c N_c \gg 2c. \]  \hspace{1cm} (4.16)

Since the quantity \( d_a N_a \) is simply the length of the crystal along the \( \vec{a}^* \) direction, etc., the above result suggests that equation 4.7 is valid if the crystal contains a large number of unit cells.

**Diffraction-Peak Intensity Profile for a Two-Dimensional Crystallite**

Equation 4.7 can be easily adapted to the case of a two-dimensional crystal, that is, a crystal which contains many unit cells along two dimensions, but only a small number along the third dimension. Because of the importance of the two-dimensional analysis to the subject matter of this thesis, the two-dimensional adaptation is shown here.

Consider a thin crystal which consists of many unit cells along the \( \vec{a} \) and \( \vec{b} \) directions, but only a few along the \( \vec{c} \) direction (as is the case with the tetracene films discussed in this thesis). We begin with equation 4.3, but this time we convert only two of the sums to integrals:

\[
S(\vec{Q}) \propto F(\vec{Q}) \sum_{n_3=1}^{N_c} e^{-i\vec{q} \cdot (n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c})} \\
\propto F(\vec{Q}) \sum_{n_3=1}^{N_c} e^{-i n_3 \vec{q} \cdot \vec{c}} \int \int d n_1 \ d n_2 \ e^{-i \vec{q} \cdot (n_1 \vec{a} + n_2 \vec{b})} \hspace{1cm} (4.17)
\]

Here, \( N_c \) is the number of unit cells, or crystal film layers, along the \( \vec{c} \) direction.

Again, we want to make a change of variables so that we can integrate over the
conventional spacial coordinates. We therefore make the transformation

\[ x = n_1 a_x + n_2 b_x, \]
\[ y = n_1 a_y + n_2 b_y. \]  

(4.18)

After the change of variables, equation 4.17 becomes

\[ S(\vec{Q}) \propto F(\vec{Q}) \sum_{n_3=1}^{N_c} e^{-i n_3 \vec{q} \cdot \vec{c}} \iint_{A_{n_3}} \frac{dA}{A_{cell}} e^{-i \vec{q} \cdot \vec{r}} \]  

(4.19)

where \( A_{cell} \) is the area of the 2-dimensional unit cell in the a-b plane, and \( A_{n_3} \) represents the area of the crystal layer with index \( n_3 \).

Therefore, for a two-dimensional crystallite, the scattered intensity as a function of the position \( \vec{q} \) with respect to a reciprocal lattice vector is given by

\[
I(\vec{Q}) \propto |S(\vec{Q})|^2 \propto |F(\vec{Q})|^2 \sum_{n_3=1}^{N_c} e^{-i n_3 \vec{q} \cdot \vec{c}} \iint_{A_{n_3}} \frac{dA}{A_{cell}} e^{-i \vec{q} \cdot \vec{r}} \]  

(4.20)

4.3.2 Peak Width versus Crystallite Size (The Scherrer Equation)

The Case of a Single, Rectangular Crystallite

Equations 4.7 and 4.20 can be used to calculate the scattered intensity profile for a crystallite of any shape, provided that the crystal contains a sufficiently high number of unit cells. It will now be shown how the crystallite size may be estimated from the width of a measured diffraction peak.
For the sake of simplicity, consider a rectangular crystallite with axes along the \( \hat{x}, \hat{y}, \) and \( \hat{z} \) directions. Starting with equation 4.7, the scattered intensity from this crystallite can be expressed as

\[
I(\vec{Q}) \propto \left| \frac{F(\vec{Q})}{V_{cell}} \right|^2 \left| \int_0^{L_x} dx \ e^{-i q_x x} \right|^2 \left| \int_0^{L_y} dy \ e^{-i q_y y} \right|^2 \left| \int_0^{L_z} dz \ e^{-i q_z z} \right|^2
\]

\[
\propto \left| \frac{F(\vec{Q})}{L_x L_y L_z} \right|^2 \left| e^{-i q_x L_x} - 1 \right|^2 \left| e^{-i q_y L_y} - 1 \right|^2 \left| e^{-i q_z L_z} - 1 \right|^2
\]

\[
\propto \left| F(\vec{Q}) \right|^2 \left( \frac{2 - 2 \cos(q_x \cdot L_x)}{(q_x \cdot L_x)^2} \right) \left( \frac{2 - 2 \cos(q_y \cdot L_y)}{(q_y \cdot L_y)^2} \right) \left( \frac{2 - 2 \cos(q_z \cdot L_z)}{(q_z \cdot L_z)^2} \right)
\]

\[
\propto \left| F(\vec{Q}) \right|^2 \left( \frac{\sin^2 \left( \frac{q_x L_x}{2} \right)}{(q_x \cdot L_x)^2} \right) \left( \frac{\sin^2 \left( \frac{q_y L_y}{2} \right)}{(q_y \cdot L_y)^2} \right) \left( \frac{\sin^2 \left( \frac{q_z L_z}{2} \right)}{(q_z \cdot L_z)^2} \right)
\]

\[
(4.21)
\]

Clearly, the peak width along any axis is independent of the crystal size along the two other axes (although this may not be true for other crystal shapes). Consider the peak width along the \( x \) direction: Numerically, the intensity is reduced by one half at

\[
\frac{q_x \cdot L_x}{2} = 1.39.
\]

\[
(4.22)
\]

Therefore, the full-width at half-maximum \( \Delta q_x \) is expressed as

\[
\frac{\Delta q_x \cdot L_x}{2} = 2.78.
\]

\[
(4.23)
\]

The result can easily be extended to the other axes. Therefore, the length of the crystal along each axis is

\[
L_x = \frac{5.56}{\Delta q_x}, \quad L_y = \frac{5.56}{\Delta q_y}, \quad L_z = \frac{5.56}{\Delta q_z},
\]

\[
(4.24)
\]
The shape factor $K$ depends on the shape of the crystallite, and has a numerical value of 0.88 for a rectangular crystallite. The above calculation can in principle be carried out, at least numerically, to obtain equations analogous to (4.25) for a crystal of arbitrary shape. Where the crystal shape is unknown, this result can be used as an approximation to obtain an estimate of the crystal size.

**The Case of Powder Diffraction**

In a common powder-diffraction experiment, all possible orientations of the crystallite are present. The resulting detectable diffraction pattern will be a set of concentric shells formed by rotating each $hkl$ diffraction peak about the origin in all directions (see figure 4.6). The width of a particular shell will therefore represent the width of the diffraction peak along the $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ direction.

The shell radius $q_{hkl}$ is given by

$$q_{hkl} = \frac{4\pi}{\lambda} \sin(\theta_{hkl}) \tag{4.26}$$

Where $\lambda$ is the X-ray wavelength. Therefore, the width $\Delta q_{hkl}$ of the shell is approximately related to the angular width $\Delta(2\theta_{hkl})$ (given in radians) by

$$\Delta q_{hkl} = \frac{4\pi}{\lambda} \cos(\theta_{hkl}) \Delta \theta_{hkl}$$

$$= \frac{2\pi}{\lambda} \cos(\theta_{hkl}) \Delta(2\theta_{hkl}) \tag{4.27}$$
Figure 4.6: Example of a diffraction pattern of concentric shells formed by revolving each \( hkl \) diffraction peak about the origin. Diffraction peaks are shown as black ovals, and the shells are shown as grey rings. The incident and diffracted wavevectors, \( \vec{k} \) and \( \vec{k}' \) are shown. The angular width \( \Delta(2\theta) \) of the shells, and the actual width \( \Delta q \) in reciprocal-space are also indicated. The angle between \( \vec{k} \) and \( \vec{k}' \) is labelled, by convention, as \( 2\theta \) since it is exactly twice the Bragg angle \( \theta \).
We can therefore relate $2\Delta\theta_{hkl}$ to the width of the crystallite along the $hkl$ direction by using equation 4.25 as an approximation

$$L_{hkl} = \frac{K\lambda}{\cos(\theta_{hkl})\Delta(2\theta_{hkl})};$$  \hspace{1cm} (4.28)

where $K$ is a numerical shape factor, on the order of 0.9, $\lambda$ is the X-ray wavelength, $\theta_{hkl}$ is the Bragg angle of the diffraction peak with index $hkl$, and $\Delta(2\theta_{hkl})$ is the angular width of the diffraction peak in radians.

Equation 4.28 is known as the Scherrer Equation [112], and is the more commonly recognized form of equations 4.25.

### 4.3.3 Diffracted Intensity from Multiple Crystallites

The above results apply to X-ray diffraction from a single crystallite. In this section, the effect of the presence of multiple crystallites on the diffracted intensity is discussed. It will be shown that, if the crystallites are coherently registered, then interference of diffracted amplitudes will result in a narrower, but more intense diffraction peak. On the other hand, we will show that if the crystallites are incoherently (or randomly) registered, then the diffracted intensities from each crystallite will simply add, and the resulting diffraction peak from the group of crystallites will have the same width as that of a single crystallite.

Consider the case of numerous crystallites with the same lattice orientation (as shown in figure 4.7), such that the diffracted intensity at a particular point in reciprocal-space has a contribution from all crystallites. Starting with equation 4.1, the total
scattered amplitude from all crystallites is

\[ S(\vec{Q}) \propto \sum_s \sum_{t \text{ in } s} F(\vec{Q}) \cdot e^{-i\vec{Q} \cdot \vec{R}_{s,t}}. \] (4.29)

Here, the first sum is taken over all crystallites (indexed by \( s \)), and the second is taken over all unit cells (indexed by \( t \)) within crystallite \( s \). \( \vec{R}_{s,t} \) is the position of unit cell \( t \) in crystallite \( s \).

The position \( \vec{R}_{s,t} \) of any unit cell can be written as \( \vec{R}_s + \vec{R}_t' \), where \( \vec{R}_s \) is the position of the crystallite, and \( \vec{R}_t' \) is the position of unit cell \( t \) with respect to some origin point within the crystallite. The amplitude is then re-written as

\[
S(\vec{Q}) \propto \sum_s \sum_{t \text{ in } s} F(\vec{Q}) \cdot e^{-i\vec{Q} \cdot (\vec{R}_s + \vec{R}_t')}
\]
\[
\propto \sum_s e^{-i\vec{Q} \cdot \vec{R}_s} \sum_{t \text{ in } s} F(\vec{Q}) \cdot e^{-i\vec{Q} \cdot \vec{R}_t'}
\]
\[
\propto \sum_s e^{-i\vec{Q} \cdot \vec{R}_s} \cdot S_s(\vec{Q}). \] (4.30)

\( S_s(\vec{Q}) \) is simply the diffracted amplitude from crystallite \( s \), and can be computed as discussed in the preceding sections.

We now begin to compute the scattered intensity. A simplified expression can be
Figure 4.7: A collection of crystallites with identical lattice orientations. The crystallite positions $\vec{R}_s$ indicate the positions of some common point within a unit cell which is contained within the crystallite, and are given with respect to a fixed origin.
obtained as follows:

\[
I(\vec{Q}) \propto |S(\vec{Q})|^2 \propto \left| \sum_s S_s(\vec{Q}) \cdot e^{-i \vec{Q} \cdot \vec{R}_s} \right|^2
\]

\[
\propto \left( \sum_{s_1} S_{s_1}(\vec{Q}) \cdot e^{-i \vec{Q} \cdot \vec{R}_{s_1}} \right) \left( \sum_{s_2} S_{s_2}^*(\vec{Q}) \cdot e^{i \vec{Q} \cdot \vec{R}_{s_2}} \right)
\]

\[
\propto \sum_{s_1} \sum_{s_2} S_{s_1}S_{s_2}^* \cdot e^{-i \vec{Q} \cdot (\vec{R}_{s_1} - \vec{R}_{s_2})}
\]

\[
\propto \sum_s I_s + \sum_{s_1} \sum_{s_2 \neq s_1} S_{s_1}S_{s_2}^* \cdot e^{-i \vec{Q} \cdot \vec{R}_{s_1,s_2}}
\]

\[
\propto \sum_s I_s + \sum_{s_1} \sum_{s_2 > s_1} \left[ S_{s_1}S_{s_2}^* \cdot e^{-i \vec{Q} \cdot \vec{R}_{s_1,s_2}} + S_{s_2}S_{s_1}^* \cdot e^{-i \vec{Q} \cdot \vec{R}_{s_2,s_1}} \right]
\]

\[
\propto \sum_s I_s + \sum_{s_1} \sum_{s_2 > s_1} \left[ S_{s_1}S_{s_2}^* \cdot e^{-i \vec{Q} \cdot \vec{R}_{s_1,s_2}} + (S_{s_1}S_{s_2}^* \cdot e^{-i \vec{Q} \cdot \vec{R}_{s_2,s_1}})^* \right]
\]

\[
\propto \sum_s I_s + \sum_{s_1} \sum_{s_2 > s_1} 2 \Re \left\{ S_{s_1}S_{s_2}^* \cdot e^{-i \vec{Q} \cdot \vec{R}_{s_1,s_2}} \right\}
\]

\[
\propto \sum_s I_s + \sum_{s_1} \sum_{s_2 > s_1} 2 \left[ \Re \{ S_{s_1}S_{s_2}^* \} \cos \left( \vec{Q} \cdot \vec{R}_{s_1,s_2} \right) + \Im \{ S_{s_1}S_{s_2}^* \} \sin \left( \vec{Q} \cdot \vec{R}_{s_1,s_2} \right) \right]
\]

(4.31)

\(\Re\{\ldots\}\) represents the real part of a complex number, and \(\Im\{\ldots\}\) the imaginary part. 

\(I_s\) simply denotes the total diffracted intensity from crystallite \(s\) alone. For simplicity, 
\(\vec{R}_{s_1,s_2} = \vec{R}_{s_1} - \vec{R}_{s_2}\) is used to represent the vector pointing to the crystallite with index \(s_1\) from that with index \(s_2\).

Again, we are interested in the intensity in the vicinity of a reciprocal lattice vector \(\vec{G}\). Therefore, as done previously, we will replace \(\vec{Q}\) with \(\vec{G} + \vec{q}\). Also, the vector difference \(\vec{R}_{s_1,s_2}\) between any two crystallites can be expressed as an integer
number of unit cells, plus a fraction of a unit cell.

\[
\vec{R}_{s_1,s_2} = n_{1,s_1,s_2}\vec{a} + n_{2,s_1,s_2}\vec{b} + n_{3,s_1,s_2}\vec{c} + \vec{r}_{s_1,s_2}
\]

\[
\Rightarrow \vec{R}_{n_{1,2}} + \vec{r}_{s_1,s_2} = \vec{R}_{n_{1,2}} + \vec{r}_{s_1,s_2} \tag{4.32}\]

where \(\vec{R}_{n_{1,2}}\) is an integer number of unit cells along each of lattice vector directions (the subscript \(n\) used to emphasize this fact), and \(\vec{r}_{s_1,s_2}\) is shorter than the dimensions of a unit cell in each direction. Equation 4.31 then becomes

\[
I(\vec{Q}) \propto \sum_s I_s + \sum_{s_1} \sum_{s_2 > s_1} 2\left[ Re\{S_{s_1}S_{s_2}^*\} \cos \left( \vec{G} \cdot \vec{r}_{s_1,s_2} + \vec{q} \cdot \vec{R}_{n_{1,2}} + \vec{q} \cdot \vec{r}_{s_1,s_2} \right) \right. \\
\left. + Im\{S_{s_1}S_{s_2}^*\} \sin \left( \vec{G} \cdot \vec{r}_{s_1,s_2} + \vec{q} \cdot \vec{R}_{n_{1,2}} + \vec{q} \cdot \vec{r}_{s_1,s_2} \right) \right] \tag{4.33}\]

Here we have used the fact that \(\vec{G}\) times an integer number of unit cells equals \(2\pi\) times an integer, and thus neglected the terms of the form \(\vec{G} \cdot \vec{R}_{n_{1,2}}\).

Finally, if we assume that each crystallite contains many unit cells, then 4.11 holds true for all scattering amplitudes of significant magnitude, and \(\vec{q} \cdot \vec{r}_{s_1,s_2}\) will have no appreciable effect. Equation 4.33 then becomes

\[
I \propto \sum_s I_s + \sum_{s_1} \sum_{s_2 > s_1} 2\left[ Re\{S_{s_1}S_{s_2}^*\} \cos \left( \vec{G} \cdot \vec{r}_{s_1,s_2} + \vec{q} \cdot \vec{R}_{n_{1,2}} \right) \right. \\
\left. + Im\{S_{s_1}S_{s_2}^*\} \sin \left( \vec{G} \cdot \vec{r}_{s_1,s_2} + \vec{q} \cdot \vec{R}_{n_{1,2}} \right) \right]. \tag{4.34}\]

Equation 4.34 gives us a way to calculate the scattered intensity from numerous crystallites of equal orientation. Notice that it is equivalently a sum of intensities.
from each individual crystallite, plus an interference term. We will now determine the effect of coherent versus incoherent registration of the crystallites.

**Coherent Scattering**

If the crystallites are registered coherently (i.e. their lattices are in-phase), then the fractional shift in registration \( \vec{r}_{s_1,s_2} \) in equation 4.34 is zero. We then have

\[
I_{\text{coherent}} \propto \sum_s I_s + \sum_{s_1} \sum_{s_2 > s_1} 2 \left[ Re\{S_{s_1}S_{s_2}^*\} \cos \left( \vec{q} \cdot \vec{R}_{n_{1,2}} \right) + Im\{S_{s_1}S_{s_2}^*\} \sin \left( \vec{q} \cdot \vec{R}_{n_{1,2}} \right) \right].
\]

(4.35)

In order to see the effect on intensity profile widths, we will calculate the ratio of the above intensity from multiple crystallites to the intensity from a single crystallite. To simplify things, we will assume that each crystallite has roughly the same shape so that we can replace each amplitude with the average amplitude \( S_{\text{avg}} \). This gives

\[
I_{\text{coherent}} \propto \sum_s I_{\text{avg}} + \sum_{s_1} \sum_{s_2 > s_1} 2 \left[ I_{\text{avg}} \cdot \cos \left( \vec{q} \cdot \vec{R}_{n_{12}} \right) + 0 \cdot \sin \left( \vec{q} \cdot \vec{R}_{n_{1,2}} \right) \right]
\]

\[
\propto \sum_s I_{\text{avg}} + \sum_{s_1} \sum_{s_2 > s_1} 2 I_{\text{avg}} \cos \left( \vec{q} \cdot \vec{R}_{n_{12}} \right).
\]

(4.36)

Therefore

\[
\frac{I_{\text{coherent}}}{I_{\text{avg}}} = \sum_s 1 + \sum_{s_1} \sum_{s_2 > s_1} 2 \cdot \cos \left( \vec{q} \cdot \vec{R}_{n_{12}} \right).
\]

(4.37)

Clearly, the ratio decreases with increasing \( \vec{q} \), indicating that the width of the
intensity profile from numerous, coherently registered crystallites will be much less than that of a single crystallite. The profile will therefore be narrower with increasing crystallite spacing.

Note that, if there are \( N \) identical crystallites, the intensity at a reciprocal lattice vector at \( \vec{q} = 0 \) will be

\[
\frac{I_{\text{coherent}}}{I_{\text{avg}}} = \sum_s 1 + \sum_{s_1} \sum_{s_2 > s_1} 2 = N + \frac{N \cdot (N - 1)}{2} \cdot 2 = N^2
\]

as would be expected for coherent scattering.

**Incoherent Scattering**

We now consider the case where the crystallites are not registered coherently (i.e. their lattices are in random registration with each other). We will examine the arguments of the trigonometric functions in equation 4.34.

Consider the term \( \vec{G} \cdot \vec{r}_{s1,s2} \), which can be written as

\[
\vec{G} \cdot \vec{r}_{s1,s2} = (h \vec{a}^* + k \vec{b}^* + l \vec{c}^*) \cdot (x_{a,1} \vec{a} + x_{b,1} \vec{b} + x_{c,1} \vec{c}) = 2\pi(h x_a + k x_b + l x_c)
\]

where the terms \( x_{a,b,c} \) are real numbers between 0 and 1. If the registration is completely random, then the \( x_{a,b,c} \) terms will have an even distribution, among all crys-
tallites, between the numbers 0 and 1, and the term $\vec{G} \cdot \vec{r}_{s1,s2}$ will satisfy

$$0 < \vec{G} \cdot \vec{r}_{s1,s2} < 2\pi \cdot \text{integer},$$

(4.40)

and will have an even distribution between these two limits. From this, we also have

$$\vec{q} \cdot \vec{R}_{n12} < \vec{G} \cdot \vec{r}_{s1,s2} + \vec{q} \cdot \vec{R}_{n12} < 2\pi \cdot \text{integer} + \vec{q} \cdot \vec{R}_{n12}.$$  

(4.41)

The term $\vec{G} \cdot \vec{r}_{s1,s2} + \vec{q} \cdot \vec{R}_{n12}$ will be distributed evenly between these limits, and thus the trigonometric functions in equation 4.34 will have an average value of zero. Therefore the interference term vanishes for incoherent registration.

We therefore have, via 4.34, in the case of multiple crystallites of equal orientation but of incoherent registration, the total scattered intensity is just the sum of intensities from each individual crystallite.

$$I_{\text{incoherent}} = \sum_s I_s$$  

(4.42)

We have therefore shown that, in the case of multiple crystallites of equivalent orientation but incoherent registration, the total peak width will be equivalent to that of a single crystallite. On the other hand, if the crystallites are coherently registered, a narrower diffraction peak will result, which will cause equation 4.25 to yield larger estimates for the single-crystal domain size.
4.4 GIXD Determination of Single-Crystal Domain Sizes and Preferred Growth Direction

In section 4.2.1 it was shown that, while the tetracene films appear uniform and well-connected in the AFM topographs, the GIXD results show that the films are actually sub-divided into crystal domains of two different lattice orientations, implying that the films are polycrystalline.

The degree of polycrystallinity of the films can have a large impact on the quality of the films as it pertains to electrical device performance. A film which consists of a high density of single-crystal domains will have a high density of domain boundaries (i.e. the interface between the domains), which is believed to limit the electrical mobility within organic thin films, as mentioned in section 1.1.

In this section, the mapped profiles of the diffraction peaks in reciprocal-space will be used to obtain information on the shapes and sizes of the single-crystal domains which comprise the films. The analysis is based on the mathematical framework developed in section 4.3.

Preferred Growth Direction of the Single-Crystal Domains

Figure 4.3b displays cross sections of a peak intensity profile, which exhibits apparent anisotropy in size for the crystalline domain. The peak width is narrowest along the \( \vec{b} \) axis. Due to the inverse relationship between peak width and single-crystal domain size, derived in section 4.3.2, this implies that the longest domain length is along the \( \vec{b} \) direction. Such domain-size anisotropy has been found in three different film thicknesses; 1.5ML, 4ML, and 12ML, indicating an intrinsic tendency of forming
the crystalline structure most favourably along the $\vec{b}$ direction. Theoretical studies on pentacene crystals show that the molecular binding energies ($E_b$) at the in-plane facets have the following relation: $E_b(010) > E_b(100) > E_b(\text{other facets})$ [63]. The corresponding growth velocity of the (010) step is thus higher than the (100) step (i.e., the growth probability along the $\vec{b}$ axis is higher than that along the $\vec{a}$ axis), leading to a longer domain length along the $\vec{b}$ axis. Because of the structural similarity between pentacene and tetracene crystals [59], the obtained domain-size anisotropy suggests similar energetics for the tetracene crystallites and indicates that molecular self-assembling plays an important role in the single-crystal domain growth.

This preference for growth may also be intuitively understood in terms of molecular contact areas. As illustrated in figure 4.8, a molecule added along the $\vec{b}$ direction has a higher area of contact with surrounding molecules than does a molecule added along the $\vec{a}$ direction. Since acene molecules in the crystal structure are held together by attractive van der Waals and electrostatic interactions [113], there will be a preference for molecular aggregation along the $\vec{b}$ direction in order to maximize molecular contact area.

**Estimating the Average Single-Crystal Domain Size**

To quantitatively evaluate the average domain sizes under different film thickness and substrate conditions, we further analyze the 2D-contour plots by removing the instrumentation broadening (a point-spread function) in the radial direction through deconvolution of the raw data and extracting the intrinsic peak profiles (see section 3.3.2 for details of this procedure). The deconvolution step is used to estimate the variance in the domain-size values from different data analysis processes. The main
Figure 4.8: An intuitive explanation for the preference of a single-crystal domain to grow along the $\vec{b}$ direction. As illustrated, a molecule added to the $\vec{b}$ surface will have a higher area of contact with surrounding molecules than if added to the $\vec{a}$ surface. Due to inter-molecular attractive forces, it should therefore be more likely to aggregate on the $\vec{b}$ surface than on the $\vec{a}$. 
conclusions presented here can also be drawn from the raw data without the deconvolution step. The extent to which deconvolution changes the quantitative results is reflected in the error estimates. As shown in section 4.3.1, both film-domain shape and size are linked to the diffraction peak profile via Fourier transform, and hence the shape and size of the detected diffraction peaks will be affected by the distribution of actual shapes and sizes of the tetracene domains within the film. The relation between the peak widths along a particular crystal axis, and the single-crystal domain sizes along that axis, is given by equation 4.25, and can be summarized in this simplified form:

\[ L \sim \frac{2\pi}{\Delta Q} \]  

(4.43)

Here, \( \Delta Q \) is the width of the diffraction peak (FWHM) along the crystal axis over which the crystal length \( L \) is measured. This is an alternate form of the well-known Scherrer equation [112]. Using this equation, we provide estimates for the average domain size along a particular crystal axis. The estimations for the average domain sizes along the \( \vec{a} \) and \( \vec{b} \) directions are listed in table 4.2.

We find that the average domain sizes (\( L_{\vec{b}} \) and \( L_{\vec{a}} \) in table 4.2) tend to increase with the film thickness from 1.5 to 4 ML, but apparently decrease for thicker films (e.g., 12 ML). These results show directly that the domain sizes are layer dependent, and illustrate two points: (1) The second-layer domains are larger than the first-layer domains, so that the average domain sizes increase with the film thickness in early growth; (2) the fact that the domain sizes decrease for the thicker films strongly suggests a clear change in the nucleation density (or growth mode) as the growth proceeds. Such domain-size changes are consistent with our earlier work, in which
Table 4.2: Table of single-crystal domain-size measurements for tetracene films of various thickness grown on 0.03° miscut Si(001) substrates. Measurements for each of the two possible lattice orientations are shown, in which the film \( \vec{b} \) direction is aligned either parallel or perpendicular to the atomic substrate steps (i.e. the substrate (110) direction). \( L_{\vec{a}} \) and \( L_{\vec{b}} \) represent the length of the domains measured along the film \( \vec{a} \) and \( \vec{b} \) directions respectively. Uncertainties are estimated to be ±10%, ±15%, and ±20% for the three thicknesses, 1.5ML, 4ML, and 12ML respectively.

<table>
<thead>
<tr>
<th>Film Thickness</th>
<th>( b \parallel ) steps</th>
<th>( b \perp ) steps</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( L_{\vec{a}} )</td>
<td>( L_{\vec{b}} )</td>
</tr>
<tr>
<td>1.5ML</td>
<td>1020Å 1400Å</td>
<td>1030Å 1300Å</td>
</tr>
<tr>
<td>4ML</td>
<td>1130Å 2200Å</td>
<td>900Å 1460Å</td>
</tr>
<tr>
<td>12ML</td>
<td>410Å 920Å</td>
<td>420Å 880Å</td>
</tr>
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</table>

we showed that the initial film (<2ML) involves certain disorder in the molecular packing, and that a significant amount of highly crystallized structure emerges at a nominal coverage of 3 ML [64]. Presumably, the initial packing disorder could be attributed to the higher density of domain boundaries (i.e., smaller domain sizes) in the first layer than in the second layer, and we believe that the maximum domain sizes are likely formed around 3-4ML.

Polycrystallinity of the Islands

Comparison of the domain sizes (\( L_b \) and \( L_a \)) and the surface topography images (figure 4.1) reveals that tetracene monolayer islands are not single crystals, but composed of numerous crystallites of the two types of single-crystal domains. The top surface island sizes in figure 4.1 are on the order of tens of micrometers in size, which is approximately two orders of magnitude larger than the average domain sizes estimated from the widths of the in-plane diffraction peaks, which are on the order of 0.1µm according to table 4.2. Such an extremely large difference in size between islands and
domains is a result of kinetic growth processes in conjunction with limited molecule self-assembling. As shown in previous works [40, 65, 114], the initial organic film growth is facilitated by a diffusion-limited-aggregation (DLA) [115] (hit-and-stick) type mechanism, and by a growth-front smoothing (island edge diffusion) mechanism at elevated temperatures. The existence of the single-crystal domains should be related to the latter (thermodynamic) mechanism, while the area density (or the size) of the domains is related to the former, which is sensitive to the kinetic growth conditions. The high deposition rate we used in order to achieve a layered film morphology [65] would thus be the primary limiting factor for the domain sizes.

Because the formation of crystalline domains is driven by thermodynamics while the formation of topographical islands may not be dominated by energetic factors, the preferred growth directions for these two structures could be different. Recent work [114, 116] with pentacene on silicon substrates shows that the islands are always elongated along the $\vec{a}$ direction\(^1\), which has been interpreted as due to kinetic preference in growth. While this kinetic result could also be true for tetracene island growth, considering the structural similarity between pentacene and tetracene crystals, our results on the domain-shape anisotropy clearly indicate that the crystalline lattice preferably grows along the $\vec{b}$ direction.

The polycrystallinity of the islands will be explored in more detail in chapter 5, in which \textit{Lateral Force Microscopy} provides more insight into the real-space distribution of crystal domains which make up the film.

\footnote{Note that the $\vec{a}$ axis here is as defined by the labelling convention used in this thesis, as described in chapter 1. The cited work uses a different crystal axis labelling convention from that used in this thesis, in which the $\vec{a}$ and $\vec{b}$ vectors are interchanged.}
4.5 GIXD of Tetracene Films on High Step-Density Substrates

In the previous sections, it was shown that tetracene films grown on the well-ordered, inert Si(001)-monohydride surface will lock into well-defined orientations with respect to the substrate, and will undergo a small compression in the lattice in order to match the periodicity of the substrate along the film $\vec{a}$ direction. This demonstrates that even an inert substrate can influence the film structure. We might therefore anticipate that substrate steps also have a large influence over the film structure.

Substrate steps are unavoidable on atomically flat crystal surfaces, and can be controlled to some extent by adjusting the miscut angle. It is therefore of practical interest to study films grown on vicinal (miscut) surfaces in order to study the effects on film structure, which may have consequences for electronic device performance.

In this section, GIXD results are presented for tetracene films grown on a substrate surface with a high step-density. The results will be compared to low step-density surfaces in order to elucidate the effect of the substrate steps on the single-crystal domains.

4.5.1 Effect of Substrate Steps on Single-Crystal Domain Sizes

In order to study the effect of the substrate steps, tetracene films were grown on a Si(001)-monohydride surface with a miscut angle of $0.3^\circ$ towards the substrate (1$\overline{1}$0) direction. With such a miscut, the average step spacing is expected to be $\sim260\text{Å}$, which is a factor of ten smaller (and hence step-density is a factor of ten larger) than
Table 4.3: Table of single-crystal domain-size measurements for tetracene films grown on high step-density, 0.3° miscut Si(001) substrates. Measurements for each of the two possible lattice orientations are shown, in which the film $\mathbf{b}$ direction is aligned either parallel or perpendicular to the atomic substrate steps (i.e. the substrate (110) direction). $L_{\mathbf{a}}$ and $L_{\mathbf{b}}$ represent the length of the domains measured along the film $\mathbf{a}$ and $\mathbf{b}$ directions respectively. The aspect ratios ($L_{\mathbf{b}}/L_{\mathbf{a}}$) are given to emphasize the difference in domain shapes produced by the two lattice orientations. Uncertainties are estimated to be $\pm 10\%$ and $\pm 15\%$ for the two thicknesses, 1.5ML and 4ML respectively.

<table>
<thead>
<tr>
<th>Film Thickness</th>
<th>$\mathbf{b} \parallel$ steps</th>
<th>$\mathbf{b} \perp$ steps</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L_{\mathbf{a}}$</td>
<td>$L_{\mathbf{b}}$</td>
</tr>
<tr>
<td>1.5ML</td>
<td>560Å</td>
<td>950Å</td>
</tr>
<tr>
<td>4ML</td>
<td>530Å</td>
<td>1040Å</td>
</tr>
</tbody>
</table>

the 0.03°-miscut substrates for which results have been presented thus far.

GIXD experiments on the high step-density, 0.3°-miscut substrate indeed show an effect on domain sizes and anisotropy. Measurements of the domain sizes (analogous to those presented in table 4.2 on page 108) are listed in table 4.3 for two film thicknesses. Notice that, on comparing these measurements with those in table 4.2, for the same coverage (4ML) films, the single-crystal domain sizes decrease sensitively with increasing miscut angle (and therefore, increasing substrate step density). Decreasing the terrace width from 2600Å to 260Å has the effect of reducing the average domain size by nearly a factor of two. However, in contrast, the top surface islands from AFM imaging appear similar in size and shape for both substrates, insensitive to the change in the substrate step density, as shown in figure 4.9a.
Figure 4.9: a) AFM topographs of a 4ML tetracene film grown on a low step-density (0.03°-miscut) Si(001)-monohydride surface (left), and a high step-density (0.3°-miscut) surface (right). There is no obvious difference in the basic film and island morphology between the two substrates. The inset in the left figure illustrates that the underlying substrate steps are visible through the film layers. b) Illustration of a lattice dislocation that is induced by the substrate steps.
4.5.2 Step-Induced Single-Crystal Domain Boundaries

To understand the apparent discrepancy between the X-ray and AFM results, we suggest that substrate steps may help to induce domain boundaries in the tetracene film. Because a Si(001) surface step is roughly 10% of the height of a single layer of upright tetracene molecules, the molecules from both sides of a substrate step are vertically shifted with respect to one another (as illustrated in figure 4.9b), which would weaken the interaction between these molecules due to the contact area being reduced. This vertical shift is evident in AFM topographs of the top film surface, through which the substrate steps are clearly visible (see inset in figure 4.9a). The visible-step image suggests that the tetracene film tends to conform to the substrate, even across substrate atomic steps. Hence a certain amount of disruption in the crystal structure may occur at substrate steps forming domain boundaries, resulting in effectively smaller single-crystal domains indicated by the X-ray results. Note that on the high-step-density substrate, our domain size estimates tend to be larger than the average terrace width of 260Å, indicating that, despite the vertical shifting in the film lattice that is induced by the substrate steps, there is still some degree of correlation in the in-plane lattice registration across the substrate steps.

4.5.3 Step Influence on Single-Crystal Domain Shape and Growth Anisotropy

We further find that the choice of step orientation can induce domain growth anisotropy. Note that in our samples, the miscut is towards the silicon (110) direction. Therefore the substrate steps separate adjacent silicon terraces which alternate between having silicon dimer rows oriented parallel and perpendicular to the steps (see section 1.3).
Figure 4.10a displays a reciprocal-space map of the diffraction peaks for a 4-ML film grown on a 0.3°-miscut substrate. From figure 4.10a, as compared with 4.3a, the step influence on domain shape is clearly seen in the shapes of the diffraction peaks. First, for domains oriented with the preferred growth direction (i.e., the $\vec{b}$ axis - see section 4.4) perpendicular to the substrate steps, the diffraction peaks (e.g., the peak labeled 1 in figure 4.10a) appear significantly more isotropic than the case shown in figure 4.3a (i.e., the aspect ratio of $L_b/L_a = 1.16$ for high miscut vs. 1.62 for low miscut - see tables 4.3 and 4.2), suggesting that the preference for growth in the $\vec{b}$ direction has been diminished by the presence of the substrate steps. Second, for domains oriented with the $\vec{b}$ axis parallel to the substrate steps, the diffraction peaks (e.g., the peak labeled 2 in 4.10a) show virtually no change in the aspect ratio (1.96) compared with the case shown in figure 4.3a (1.95), indicating that the preferred growth direction has been preserved for these domains. Lastly, the aspect ratio difference for the two types of domains dramatically increases with the miscut angle, from 0.33 (=1.95-1.62) for a 0.03°-miscut substrate to 0.80 (=1.96-1.16) for a 0.3°-miscut substrate. In other words, significant step anisotropy in the substrate substantially enhances the shape difference between the two types of domains, depending on the preferred domain growth direction relative to the substrate step orientation.

These observations are consistent with the hypothesis that the substrate steps may help to induce domain boundaries. As illustrated in figure 4.11, when the step spacing (or the terrace width) is much larger than the average domain sizes (as in the case of the low-miscut substrate), the aspect ratios for the two types of domains tend to be similar, indicating that molecular self-assembling in the domain formation is not significantly influenced by the steps here. When the step spacing is comparable
Figure 4.10: a) Two-dimensional reciprocal-space map of measured GIXD peaks for a 4ML tetracene film grown on a high step-density (0.3° miscut) Si(001)-monohydride surface. The contour plots are enlarged in a scale of 15:1. Substrate steps and lattice orientations are indicated in the upper left corner, and the projected position of the bulk silicon (111) peak is indicated with a blue star. The red and green dashed lines indicate the two sets of reciprocal-space unit cells which correspond to the two orthogonal lattice orientations. The projections of the reciprocal-lattice vectors $\vec{a}^*$ and $\vec{b}^*$ onto the a-b plane are also indicated. b) Cross sections of the numbered peaks, labelled by 1 and 2. Notations and resolutions are as in figure 4.3.
to the domain size (as in the case of the high-miscut substrate), domains oriented with the $\vec{b}$ axis (indicated with arrows in the figure) parallel to the steps are not prevented from growing along their preferred growth direction; however, domains oriented with the $\vec{b}$ axis perpendicular to the substrate steps would have a certain probability to be confined in the preferred growth direction, as shown by a more isotropic domain shape, indicating that the substrate roughness inevitably plays a role in the domain growth. The domain-shape anisotropy shown is closely related to the choice of miscut direction (i.e. the choice of step orientation), even though the two dominant orientations of the film lattice are fixed with respect to the substrate lattice (due to the one-dimensional registry with the substrate). Presumably, one may control the domain shapes by the step orientation to some degree.

## 4.6 Chapter Summary

In this chapter, GIXD data were used to measure the in-plane single-crystal domain changes in size and shape for a tetracene film on the silicon(001)-monohydride surface, as a function of film thickness and substrate step density. The results reveal that the film is commensurate with the substrate along the $\vec{a}$ direction of the tetracene lattice (i.e., the longer basis vector of the a-b plane unit cell), in agreement with our previous study [64]. On comparison of the single-crystal domain sizes with AFM images, it is demonstrated that a single-crystal domain in these films can be orders of magnitude smaller than a surface island. Two-dimensional reciprocal-space mapping of the diffraction peaks shows an anisotropy in the domain shape with a preferred growth along the $\vec{b}$ direction (i.e., the shorter basis vector of the a-b plane unit cell), consistent with the energetics of molecular self-assembling. For low-miscut
Figure 4.11: Schematic illustrations of a possible step-density influence on the domain formation. A double arrow for each crystallite indicates the $\vec{b}$ axis. Note that in our samples, the miscut is towards the silicon (1\overline{1}0) direction.
substrates, the domain sizes increase with the coverage initially, and decrease after a certain thickness. The domain sizes and anisotropy can be influenced by the substrate steps, which has been interpreted such that the steps have a certain probability to introduce domain boundaries at the first layer and may affect the homoepitaxial layers grown above, influencing several monolayers adjacent to the substrate, which is highly relevant to the nature of the accumulation layer in organic field-effect transistors.

In the next chapter, more insight into the properties of the domains which comprise the films will be obtained by use of Lateral Force Microscopy.
Chapter 5

Real-Space Imaging of the Film Domain Structure by Lateral Force Microscopy

In chapter 4, GIXD was used to obtain structural information pertaining to the tetracene films. Information such as lattice structure, lattice orientation, and single-crystal domain size was determined. However, a significant limitation of the GIXD experiments is that they only yield reciprocal-space information, and provide no details on the real-space domain structure of the films.

In this chapter, lateral force microscopy (LFM - as described in section 2.2) is used to obtain real-space information to complement the reciprocal-space data provided by the GIXD experiments. It is shown that images produced by LFM reveal contrast that reflects the film lattice structure and orientation, and can therefore be used to gain real-space insight into the domain structure of the films. The results are inter-
preted, and possible physical mechanisms that may be responsible for the contrast are discussed. Images obtained for films grown on high step-density substrates are also analyzed in order to determine the effect of substrate steps on the domains.

5.1 Observation of Major Domains in the TSM Images

The samples presented here were prepared using the procedure described in section 4.1. Figure 5.1 presents a set of AFM images for a 4ML tetracene film grown on a 0.03°-miscut Si(001) substrate. The AFM topograph is shown along with the corresponding TSM image, both obtained simultaneously at the same film location.

In the topograph of figure 5.1, we see the familiar island shapes that we have previously reported [64] and which were described in section 4.2.1. The long-axes of these islands are dominantly oriented along the substrate (110) and (110) directions (i.e. parallel or perpendicular to the silicon dimer rows which were discussed in section 1.3).

In the corresponding TSM image, the islands are not clearly visible. Instead, a network of domains appears (hereafter referred to as the “major domains”, as they will later be shown to have sub-structure). These major domains are on the order of tens of micrometers in size, and are only visible in the TSM images (they are completely invisible in topographs and FFM images). The vast majority of the major domains appear in one of two shades, being either light or dark, corresponding to a positive or negative twist signal, as explained in section 2.2.
Figure 5.1: AFM topograph (left) and corresponding TSM image (right) of a 4ML tetracene film grown on a $0.03^\circ$ miscut Si(001) surface. The major domains are seen only in the TSM image.
5.1.1 Dependence of the Major-Domain Contrast on Scan Direction

In the TSM images, there is an apparent dependence of the major domain contrast on the scanning direction of the AFM tip. Consider figure 5.2, which presents four TSM images taken at the same film location, but with different scan directions. The best contrast occurs when the tip scans at a 45° or 135° angle with respect to the substrate (110) direction (which has been shown in chapter 4 to coincide with the film $\vec{a}$ or $\vec{b}$ directions). The contrast inverts when the scanning orientation is rotated by 90° (i.e. when rotated from 45° to 135°), and vanishes when scanning at 0° or 90°.

In general, the TSM signal has been found to have 180° symmetry, such that if the sample is rotated by 180° with respect to the cantilever, each domain will produce the same twist signal. This can be inferred from the images in figure 5.3, which show that the TSM signal obtained during backward scanning is inverted, about some common equilibrium value, with respect to the signal obtained during the forward scan. This result is expressed by the following equation:

$$\left( TSM_{\text{forward}}(\phi) - c \right) = - \left( TSM_{\text{backward}}(\phi) - c \right) \quad (5.1)$$

Here, $c$ represents the equilibrium value. The fact that the twist signals depend on the scanning direction $\phi$ is reflected in the equation. Since a negative twist (measured about the equilibrium point) while scanning backwards is equivalent to a positive twist while scanning forwards in the opposite direction (as illustrated in figure 5.4),
Figure 5.2: TSM images of a particular location on a 4ML tetracene film grown on 0.03°-miscut Si(001). Two major domains of different shades are numbered in each image for easy comparison of the images. The diagram below each image illustrates the cantilever and scanning direction relative to the substrate. The best contrast in the major domains appears at scan directions of 45° and 135° with respect to the substrate (110) direction. Very low contrast in the major domains is observed at 0° and 90° scan directions, and the contrast is inverted when the scan direction is rotated from 45° to 135° (i.e. domain 1 changes from dark to light, and 2 changes from light to dark).
we also have the following equation:

\[
(TSM_{\text{backward}}(\phi) - c) = -(TSM_{\text{forward}}(\phi + 180^\circ) - c) \tag{5.2}
\]

Combining equations 5.1 and 5.2 results in;

\[
TSM_{\text{forward}}(\phi) = TSM_{\text{forward}}(\phi + 180^\circ). \tag{5.3}
\]

This proves that the TSM signal for our tetracene films does, in fact, have 180° rotational symmetry\(^1\).

We now desire to compare the signals yielded by the various domains for different cantilever orientations. However, this analysis is simplified if we first define the TSM hysteresis signal as the difference in the measured twist signals between the forward and backward scans:

\[
TSM_{\text{hyst}}(\phi) = TSM_{\text{forward}}(\phi) - TSM_{\text{backward}}(\phi) \tag{5.4}
\]

The hysteresis signal simplifies the discussion by eliminating the need to distinguish between the forward and backward scan images, and it eliminates any instrumental offset in the twist signal (i.e. the equilibrium value ‘c’ discussed above). Since equation 5.1 applies to our films, the expression for the hysteresis can simplified as

\(^1\)This point could, in principle, be proven more directly, simply by rotating the sample 180° and imaging at the same film location. However in practice this is difficult since the equilibrium point often changes (especially when the tip disengages from the surface), and since the repeated imaging necessary to find the same film location often changes the measured signal.
Figure 5.3: TSM images demonstrating the inversion of contrast that occurs during backward scanning. a) Shown are the AFM topograph (left) and corresponding TSM images during the forward trace (center) and backward trace (right). The diagrams below the TSM images represent the cantilever motions. b) Line profiles showing the measurements taken during forward trace (blue) and backward trace (red). The profiles were taken at the positions indicated by the blue and red lines in figure ‘a’. The black line indicates the average of the two traces (i.e. the equilibrium value), demonstrating that the backward-scan signal is simply the reflection of the forward-scan signal about the equilibrium value.
Figure 5.4: Illustration of the relation between twist signals obtained during forward or backward scanning: a) Scanning backward at cantilever orientation $\phi$ results in a counterclockwise twist (looking along the cantilever axis) due to the lateral force exerted on the tip by the surface. b) When scanning forward at cantilever orientation $\phi + 180^\circ$, the same force results in clockwise twisting. The two scenarios result in equal twisting forces, but in opposite directions with respect to the cantilever, thus validating equation 5.2
follows:

\[
TSM_{\text{hyst}}(\phi) = (TSM_{\text{forward}}(\phi) - c) - (TSM_{\text{backward}}(\phi) - c)
\]

\[
= (TSM_{\text{forward}}(\phi) - c) + (TSM_{\text{forward}}(\phi) - c)
\]

\[
= 2(TSM_{\text{forward}}(\phi) - c)
\] (5.5)

Therefore the TSM hysteresis signal is simply twice the amount that the forward twist signal differs from the equilibrium value. Naturally, due to equation 5.3, the TSM hysteresis signal will also have 180° rotational symmetry.

The TSM hysteresis images provide evidence that the two types of major domains are actually the same structure, but oriented orthogonally to each other. For instance, consider the set of hysteresis images presented in figure 5.5, along with the line profiles taken at the locations indicated by the dashed lines. The images show that, when the scan direction is rotated by 90°, the measured hysteresis corresponding to the two domains is reversed. That is, when the scan angle \( \phi \) is changed from 45° to 135°, the light domain becomes dark, and the dark one becomes light. This observation is corroborated by the line profile shown at the bottom of figure 5.5, in which it can be seen that the hysteresis values yielded by the two domains are approximately interchanged under this 90° rotation (Note that exact reversal of the hysteresis values is unlikely. See footnote for details.\(^2\)). This shows that the two domains each exhibit the same hysteresis behaviour as the other when rotated by 90°, and is therefore strong evidence that the two domains are orthogonal orientations of the same lattice.

\(^2\)Exact reversal is unlikely for three reasons: 1) This would require the sample to be rotated by exactly 90°, which is difficult to do precisely with our apparatus. 2) To locate the same film location after rotating requires repeated imaging, which has been seen to gradually damage the film, and change its contrast properties. 3) The imaging properties of the tip are not constant, often varying from image to image.
5.1.2 Effect of the Major Domains on Island Orientation

The major domains apparently determine the orientation of the islands seen in the AFM topographs. As seen in figure 5.6, all of the islands contained within a single major domain have the same long-axis orientation. Furthermore, the light-shaded major domains produce islands that are orthogonally oriented to the islands in the dark-shaded major domain.

The fact that the islands contained within different major domains are orthogonal is in direct agreement with the results of section 5.1.1, in which it was found that the major domains themselves are just orthogonal orientations of the same lattice structure. This result also demonstrates that the island orientation is linked to the lattice orientation.

5.1.3 Physical Interpretation of the Major Domains

Naturally, the two orthogonal orientations of major domains that were observed in the TSM images can be associated with the two orthogonal lattice orientations that were detected in the GIXD results presented in chapter 4. Therefore, TSM imaging has provided us with a real-space representation of domains of uniform lattice orientation.

The crystallographic axes of the lattices of the major domains may be inferred from the results of previously published work. As mentioned in section 4.4, the relation between the orientations of the island long-axis and that of the crystal lattice has been established in a study of pentacene films grown on silicon surfaces [116]. In that study, low-energy electron-diffraction was used to determine the lattice orientation of
Figure 5.5: Two TSM hysteresis images of the same film location, but with different TSM scan directions. The red and green line profiles at the bottom represent the measured hysteresis corresponding to the respectively coloured dashed lines in the TSM images. When the scan direction $\phi$ is rotated by $90^\circ$, the hysteresis signals are approximately interchanged (note that exact reversal of the hysteresis measurements is unlikely due to experimental variations - see footnote on page 127). This strongly suggests that the two types of major domains are actually the same structure, but with orthogonal orientations. Note that the TSM images shown here have been processed to enhance the contrast. However, the line profiles were taken from the raw, unprocessed data.
Figure 5.6: AFM topograph (left) and corresponding TSM image (right) demonstrating the effect of the major domains on island orientation. In the topograph, the islands on the left half of the image are contained within a dark major domain (seen in the TSM image), while the islands on the right are on a light domain. The orientations of the island long-axes, indicated by green arrows, are uniform within each major domain. The axes shown on the TSM image indicate the directions of the film lattice vectors, which are inferred from previous published results [116], as described on page 131.
individual pentacene islands, and it was found that the island long-axis was parallel to the film $\vec{a}$ axis, which is perpendicular to the direction of highest binding energy [63]. The authors therefore inferred that kinetic, rather than thermodynamic, processes dominate the growth of islands.

Since the structure and surface energetics of pentacene and tetracene are similar [63], these results can be extrapolated to our tetracene films, allowing us to assign lattice orientations to the individual major domains, as shown by the overlaid axes in the TSM image of figure 5.6. These axes are oriented such that the $\vec{a}$ direction is parallel to the long-axis of the islands contained in each respective major domain. The overlay in the figure illustrates the molecules in their inferred orientations.

### 5.1.4 TSM Contrast Mechanism of the Major Domains

Despite the simplicity of the TSM technique, few existing studies have employed it for the purposes of domain imaging [77–82,117,118]. All existing literature attributes the TSM contrast to domains of varying lattice orientation, as we do in this work. However, there is currently no clear consensus on the physical origin of the TSM twist signal. For completeness of the discussion, the main theories are presented here.

An attempt to explain the twist signal origin was first made by Kalihari and co-workers [79, 80]. In their work, they observe similar domains in pentacene films grown on an isotropic SiO$_2$ surface, but with multiple lattice orientations. To explain the contrast mechanism, they propose an “elasticity model” in which the twist signal originates from the elastic anisotropy of the film crystal lattice, and that the orientation-dependence of the contrast arises as a result of the different elastic re-

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$^3$This is using the axis labelling convention used in this thesis, defined in chapter 1, and not that of the cited work.
sponse of the film to the tip-induced shear strain along different crystallographic directions. They show that a simple mechanical model based on the theory of linear elasticity [119], when applied to anthracene (a molecule of three benzene rings which has a crystal structure similar to pentacene and tetracene, and for which the elastic constants are known [120]), results in the same qualitative relationship between twist signal and scan direction that they measured experimentally. They suggest that this qualitative agreement is evidence of the validity of their model.

A competing theory of the origin of the TSM contrast was proposed by Campione and Fumagalli [82]. They show that, while the elasticity model successfully predicts the TSM contrast behaviour for pentacene (as shown by Kalihari and co-workers), it does not work when applied to their system of study, that is, thin films of potassium hydrogen phthalate. They instead propose a “corrugation model”, in which the twisting forces on the AFM tip arise from the atomic-scale corrugations of the crystal surface, and the transverse forces that they exert on the tip during scanning. They also argue that the twist-signal behaviour observed by Kalihari and co-workers for pentacene [79] can be successfully explained by this model.

Thus far, our attempts to narrow down these possibilities remain inconclusive. It is possible that both the elasticity model and the corrugation model contribute significantly to the TSM twist signal. This issue is deferred for future work to resolve.

5.1.5 Polycrystallinity of the Major Domains

It has now been established that the two dominant shades of the major domains in the TSM images represent the two orthogonal crystal lattice orientations that are known to be present from the GIXD results of chapter 4. However, the TSM images reveal
that the major domains are on the order of tens of micrometers in size, which is about two orders of magnitude larger than the single-crystal domain sizes reported in table 4.2 (typically $\sim 0.1\mu m$). This suggests that the major domains are not single-crystals, but have some sub-structure. This issue will be explored further in the next section.

## 5.2 Observation of Sub-Domains in the TSM and FFM Images

On examination of smaller-scale images of the tetracene films, it is found that the major domains consist of another type of smaller domain (hereafter referred to as “sub-domains”). As shown in figure 5.7, these domains make up the major domains, and exhibit an elongated, “tiger-skin”-like pattern.

Like the major domains, the sub-domains exist in two dominant shades in the images, being either light or dark. However, unlike the major domains, the sub-domains are visible in both types of LFM image, both TSM and FFM. This implies that the tip experiences a difference in friction force as it slides across a sub-domain boundary (recall from the discussion in section 2.2 that FFM images are sensitive to conventional friction forces, while TSM images are sensitive to variations in transverse forces).

The directions of elongation are in good agreement with the physical interpretation of the major domains that was developed in section 5.1. For instance, it is immediately apparent in the images that the direction of elongation of the sub-domains is uniform within a particular major domain. Furthermore, the sub-domains contained in the lighter-shaded major domains are elongated in an orthogonal direction to those of
Figure 5.7: AFM topograph (left) and corresponding TSM (center) and FFM (right) images revealing the presence of sub-domains in the tetracene films. The sub-domains can be seen in both the TSM and FFM images, while the major domain boundary can only be seen in the TSM image. Green arrows indicate the preferred direction of elongation of the sub-domains, which are perpendicular to the island elongation direction (red arrows) within each respective major domain.
the darker-shaded major domains. This is further confirmation that the two types of major domains are, in fact, orthogonal orientations of the same film structure, as described in section 5.1.3.

5.2.1 Dependence of the Sub-Domain Contrast on Scan Direction

As was the case with the major domains, the sub-domain twist signal also varies with scan direction. This scan direction dependence is observed in both TSM and FFM images, and suggests that the twist signal produced by these domains is also related to the crystal lattice orientation.

This orientation dependence is demonstrated in figure 5.8. In the FFM images, the sub-domain contrast is at its maximum when scanning at a 45° (or 135°) angle with respect to the substrate (110) direction, but disappears almost entirely when scanning at 0° (or 90°). The behaviour is opposite in the TSM images, in which the contrast is weakest (but still clearly visible) at a 45° (and 135°) scan direction, but is strongest at 0° (or 90°).

5.2.2 Physical Interpretation of the Sub-Domains

The interpretation of the sub-domains seen in the LFM images is somewhat less straightforward than that of the major domains, and domains of this type have, to our knowledge, not been observed before. However, a clue may be found in the GIXD data that was presented in chapter 4. As explained in section 4.2.1, a significant amount of domains exist in the film which are “upside-down” with respect to each other. These orientations may be obtained by rotating the lattice by 180° about the $\vec{a}$,
Figure 5.8: FFM and TSM images showing the dependence of the sub-domain contrast on scan direction. In the top row, the FFM image and corresponding TSM image were taken at the same film location with a scan direction of $0^\circ$ with respect to the substrate $[1\bar{1}0]$ direction. The FFM image shows almost no sub-domain contrast, while very well-defined contrast appears in the TSM image. In the bottom row, the FFM images and TSM images for another film location are shown in which the scan direction is $45^\circ$. For this scan direction, both the FFM and TSM images reveal moderate sub-domain contrast.
\vec{b}, or \vec{c}^* axes, as shown in figure 5.9 (here, the vector \vec{c}^* represents the reciprocal-lattice vector that is parallel to the surface normal, and perpendicular to the a-b plane). It can be seen in figure 5.9 that, while the in-plane periodicity of the various lattice orientations is the same, the effective molecular tilt direction (indicated by the green arrows) is different, and can point in one of four possible directions. It is therefore conceivable that each of the major domains seen in the TSM images actually consist of many smaller domains of varying directions of molecular tilt.

If all four of these lattice orientations exist in each major domain, as the GIXD data suggest, then these varying orientations of molecular tilt may be responsible for the observed sub-domain contrast in the TSM and FFM images. In this case, the various molecular tilt directions may have the effect of producing different frictional and transverse forces in the FFM and TSM images respectively, hence resulting in the observed contrast. These types of domains of varying molecular tilt direction have previously been observed in pentacene films using low-energy electron microscopy (LEEM) [121].

To our knowledge, no studies of the influence of molecular tilt on the FFM twist signal for acene molecules, such as tetracene, have been published to date. However, a few studies show that there is such an influence in films consisting of chain-like organic molecules, both experimentally [83–85, 122–125] and theoretically [126, 127]. For example, Liley and co-workers [83] have found that the total measured friction is anisotropic, being highest when scanning perpendicularly to the molecular tilt direction, and lowest when scanning with or against the molecular tilt. They further show that friction is only slightly asymmetric, meaning that the forward and backward scans yield slightly different friction measurements. The measured asymmetry is
Figure 5.9: A proposed interpretation of the sub-domains, in which different domains are produced by simple 180° rotations about the $\vec{a}$ or $\vec{b}$ axes, or about the surface normal (which is parallel to the $\vec{c}^*$ axis). Such rotations effectively result in a change in the molecular tilt direction (indicated by a green arrow), while preserving the in-plane lattice parameters. As shown, four different molecular tilt directions are possible (numbered 1 through 4 in the figure).
highest when scanning parallel to the tilt direction, however the magnitude of the asymmetry is small compared to the total measured friction.

It has been theorized that the higher friction measurement when scanning perpendicularly to the molecular tilt direction is due to a higher lateral compliance of the film along this direction (i.e. the molecules deflect more easily along the direction transverse to the tilt direction), which allows more energy to be dissipated during tip sliding, resulting in higher friction [126]. The higher compliance could also lead to increased contact area between the tip and sample, which is also believed to result in higher friction [128, 129]. We propose that this same effect, if applicable to our tetracene films, successfully explains how the domains of various molecular tilt directions result in the observation of sub-domains in the FFM images. For example, consider figure 5.10, which depicts the four possible molecular tilt domains which are hypothesized above to exist within a particular major domain in the tetracene film. Due to the different molecular tilt directions, each domain could possibly produce a different FFM twist signal. However, if the friction asymmetry is low (as observed in the system studied by Liley and co-workers [83]), then domains which have opposite molecular tilts (i.e. the boxed pairs in figure 5.10) will produce essentially the same twist signal, and would be indistinguishable in the FFM images. Therefore, the four molecular tilt domains would actually appear as two in the FFM images, which matches our experimental observations.

This friction versus molecular tilt relationship also explains the dependence of sub-domain contrast on scan direction that we have observed. For instance, if the tip is scanning at a 45° angle with respect to the film $\vec{a}$ or $\vec{b}$ axes, as shown in figure 5.10, then it will be scanning nearly parallel to the molecular tilt of boxed pair #1
Figure 5.10: Illustration of the proposed mechanism by which domains of different molecular tilt can be observed in the FFM images. The boxed pairs represent domains of opposite molecular tilt, which cannot be distinguished due to the 180° rotational symmetry of the FFM signal, as described in the text. Therefore, the twist signal depends only on the absolute angle between the scan direction (red dotted lines) and the molecular tilt azimuth (green lines).

When the tip is scanning at $\phi = 45^\circ$ with respect to the film $\vec{a}$ or $\vec{b}$ direction, the scan direction is nearly parallel to the tilt azimuth for domain pair #1 (resulting in low friction), and nearly perpendicular to the tilt azimuth for pair #2 (resulting in high friction). Therefore the two pairs will yield different twist signals, resulting in high sub-domain contrast for this scan direction. On the other hand, if the tip scans at an angle of $\phi = 0^\circ$ or $90^\circ$, the scan direction makes the same angle with the tilt azimuth of both domain pairs (resulting in medium friction), and thus no sub-domain contrast is observed for these scan directions.
in the figure, resulting in a low friction signal. On the other hand, the tip will be
scanning nearly perpendicularly to the tilt direction for boxed pair #2, resulting in
a high friction signal. Therefore, the two domain pairs will be highly contrasted in
the FFM images when the scan direction is \(45^\circ\), as was observed in our experiments.
On the other hand, if the tip scans parallel to the \(\vec{a}\) or \(\vec{b}\) axis, then the scan vector
will make the same angle with the tilt direction of all four domains, thus producing
the same friction signal, and producing no sub-domain contrast, as observed in our
experiments.

The effect of molecular tilt on the TSM twist signal is less easy to visualize,
and to our knowledge no work has been published which studies this relationship.
However, since the sub-domains are visible in both FFM and TSM images, it is
reasonable to assume that the TSM twist signal is coupled to the frictional force that
was responsible for the FFM contrast. Under this assumption, the TSM contrast can
also be explained. For instance, consider figure 5.11. As in figure 5.10, the boxed
pairs represent domains of opposite molecular tilt, which cannot be distinguished due
to the \(180^\circ\) rotational symmetry of the friction signal. The blue lines indicate the
direction of highest friction, which is transverse to the molecular tilt direction. For a
TSM scan direction of \(\phi = 0^\circ\) (or \(\phi = 90^\circ\)), the tip crosses these lines from opposite
sides for each boxed pair. This asymmetry results in opposite twisting forces, and
high contrast in the TSM images (in agreement with the TSM images). On the other
hand, for a scan direction of \(45^\circ\), the tip scans nearly perpendicularly to the high-
friction lines in boxed pair #1, and nearly parallel to those of boxed pair #2. These
high-symmetry directions (with respect to the friction behaviour) would result in low
twisting forces, and hence low contrast in the TSM images (again, in agreement with
the TSM images).

### 5.2.3 Polycrystallinity of the Sub-Domains

The size of the sub-domains in the TSM and FFM images range in size from about 0.1\( \mu \)m to 5\( \mu \)m. The sub-domains are therefore closer in size to the single-crystal domain sizes estimated from the GIXD data (see table 4.2 on page 108) than are the major domains, and may therefore be more representative of the actual single-crystal domains in the film. However, the fact that the sub-domains are up to an order of magnitude larger than the GIXD-determined domain sizes suggests that the sub-domains are also polycrystalline.

The polycrystallinity of the sub-domains fits well into the physical picture developed above in section 5.2.2, in which it was argued that the sub-domains represent domains of different molecular tilt directions. However, domains of opposite tilt are indistinguishable in the TSM and FFM images, suggesting that the sub-domains may be further divided into domains of opposite tilt which are not detectable in the TSM or FFM images. This would explain why the sub-domains in the TSM and FFM images are larger than the GIXD-determined size estimates.

In addition to the existence of these invisible domains of opposite molecular tilt, it is also possible that some other form of invisible disorder is responsible for the effectively smaller single-crystal domain sizes determined by GIXD. For example, lattice dislocations (i.e. shifts in the registration between adjacent domains, possibly caused by the coalescence of domains that have been growing separately) would also be invisible in the TSM and FFM images, and would thus reduce the single-crystal domain sizes as determined by the GIXD experiments, without reducing the apparent
Figure 5.11: The proposed mechanism by which domains of different molecular tilt can be observed in the TSM images. As in figure 5.10, the boxed pairs represent domains of opposite molecular tilt, which cannot be distinguished due to the 180° rotational symmetry of the friction signal. The blue lines indicate the direction of highest friction, which is transverse to the molecular tilt direction.

For a TSM scan direction of $\phi = 0^\circ$, the tip crosses these lines from opposite sides for each boxed pair. This asymmetry results in opposite twisting forces, and high contrast in the TSM images. On the other hand, for a scan direction of $45^\circ$, the tip scans nearly perpendicularly to the high-friction lines in boxed pair #1, and nearly parallel to those of boxed pair #2. These high-symmetry directions (with respect to the friction behaviour) would result in low twisting forces, and hence low contrast in the TSM images.
sub-domain sizes in the TSM and FFM images.

5.2.4 Elongation of the Sub-Domains

In light of the physical understanding of the sub-domains developed above, the elongation of the sub-domains is naturally explainable in terms of surface energetics. In section 5.1.3 it was argued, with reference to a previous study [116], that the long-axis of the film islands are oriented along the film \( \vec{a} \) direction. The sub-domains, which are elongated perpendicularly to the island long-axes, as seen in figure 5.7, are therefore elongated along the \( \vec{b} \) direction, which is the surface of highest energy [63].

The elongation along the direction of highest energy is expected for single-crystals since the interaction strength between molecules is the greatest along this direction, which renders it less energetically favourable for domain boundaries to form. The higher interaction strength between molecules is attributable to the higher contact area between molecules along this direction, as illustrated in figure 4.8.

5.3 Domain Structure of the First and Second Film Layers

TSM and FFM images of the first and second film layers present some significant differences from the upper layers. Figures 5.12, a, b and c, respectively display a topograph along with corresponding FFM and TSM images of a 1.5 monolayer film. While the major domains are still clearly visible in the first layer, no sub-domain contrast can be seen. This suggests that the lower layers still maintain the same crystal lattice structure that was responsible for the major domain contrast
properties in the upper layers. However, the lack of visible sub-domains suggests that some underlying difference exists.

The lack of ability to image the sub-domains in thin films may be indicative of some difference in the film structure of the lower layers. As has been mentioned, evidence that the thinner tetracene films are of a different structure has been published in our previous work [64], in which NEXAFS spectra showed that a structural transition in the film likely occurs during film growth at about the time of completion of the third monolayer. This coverage-dependent structural transition comes in the form of a change in the molecular orientation and/or tilting angle within the film. This change may occur without affecting the in-plane lattice parameters, and would therefore be consistent with the lattice parameter measurements presented in section 4.2.2 which showed that the lattice parameters do not change with film thickness (up to the thicknesses measured). It is therefore conceivable that the different structure in the first layers might be responsible for the lack of sub-domain contrast.

A second possibility which may make sub-domain imaging a practical difficulty for 1-2ML films is a lower film rigidity. This characteristic may take effect in addition to, or as a result of, the differing film structure described above. It has previously been shown in other thin film systems [129] that higher friction forces are measured in FFM imaging for thinner films (1-2ML). This effect has been explained in terms of low rigidity of the thin films, which causes the film to “pucker” during scanning, leading to a higher tip-surface contact area, and hence a higher friction force. For thicker films, a greater rigidity would presumably reduce this effect.

This effect is also observed in our tetracene films. Figure 5.12d presents a line-scan of the signal “hysteresis” corresponding to the line drawn in the FFM image of

145
Figure 5.12: a) AFM topograph of second-layer islands growing on the completed first layer. b) FFM image corresponding to figure ‘a’. c) TSM image of the same location. Note that a major domain boundary is visible, but no sub-domains can be seen in any of the images. d) Line scan showing the hysteresis signal corresponding to the white, dashed line indicated in figure ‘b’. A lower FFM hysteresis signal is measured on the second-layer islands than on the completed first layer, indicating a lower friction force experienced by the tip on the second layer.
The hysteresis (equation 5.4) is defined as the difference in twist signals measured during forward and backward scanning of the cantilever, and is a direct measure of frictional force because it represents the difference in twist during forward and backward scanning. If there is low friction, both the forward and backward traces will result in low cantilever twist, and the measured hysteresis will be small. In the case of high friction, forward and backward scanning will cause large cantilever twisting in opposite directions, leading to a large difference between the forward and backward trace signals, and hence a larger hysteresis. As can be seen in figure 5.12d, the hysteresis is over two times larger for the first layer than the second, showing that the first layer does in fact yield higher friction.

The differences in the LFM images between the lower and upper layers may also help to explain why the sub-domains have not been observed by Kalihari and co-workers [78–80]. Those results applied to a single monolayer of pentacene, and therefore may not have exhibited sub-domain structure simply because those films were not thick enough.

### 5.4 Influence of Substrate-Steps on the Domain Structure

#### Step Influence on the Sub-Domains

LFM images of the tetracene film domain structure reveal evidence that the substrate steps help to induce boundaries in the sub-domains, in addition to the single-crystal domain boundaries discussed in chapter 4. Shown in figure 5.13a is a high-resolution AFM topograph of a 4ML tetracene film. As was the case in figure 4.9, the substrate
steps can be clearly seen in the topograph through the tetracene layers. On comparing the topograph of figure 5.13a with the corresponding TSM image in figure 5.13b, the clear influence of the substrate steps over the sub-domains is seen. In the figure, dotted lines are overlaid onto the TSM image to indicate the positions of the substrate steps, as determined from the topograph. In many places (examples indicated by green arrows), the sub-domain boundaries conform precisely to the contours of the substrate steps, demonstrating that there is significant probability for the sub-domain boundaries to form at the steps.

As was explained in section 5.2.3, the sub-domains in the LFM images do not exactly represent the single-crystal domains studied in the GIXD experiments. However, the argument used to explain how substrate steps induce single-crystal domain boundaries may also apply to sub-domain boundaries. That is, the reduced inter-molecular interaction that results from the reduced molecular contact area at the steps, illustrated in figure 4.9b, leads to a higher probability of domain boundary formation.

It is apparent in the TSM and FFM images that the shape and size of the sub-domains depends on their orientation with respect to the substrate steps. For example, figure 5.14b shows a TSM image for a low step-density, 0.03°-miscut substrate, in which the sub-domains are visible. In the image, the sub-domains which are elongated perpendicularly to the substrate steps are shorter and seemingly more disordered than those which are elongated parallel to the steps. This effect can be understood in the context of the physical picture of step-induced domain boundaries that has been described thus far, and the model of figure 4.11 may be applied to the sub-domains as well. Since domain boundaries have a higher probability of forming at the substrate steps.
Figure 5.13: a) High-resolution AFM topograph, and; b) TSM image of a 4ML tetracene film grown on a low step-density substrate. The substrate steps can be seen in the topograph through the film layers. The positions of the steps, determined from the topograph, are overlaid on the TSM image, revealing that the sub-domain boundaries conform to the steps in many places (examples of this are indicated by green arrows).
steps, domains will effectively be shortened in the direction perpendicular to the steps. It was shown using GIXD and LFM data, in sections 4.4 and 5.2.4 respectively, that the single-crystal domains and sub-domains each show a preference for growth along the film $\vec{b}$ direction. Therefore, for domains with lattice orientations such that $\vec{b}$ is aligned perpendicular to the steps, the preference for growth along the $\vec{b}$ direction is interrupted by the domain boundaries which are induced by the steps. This results in domains which are shorter with a lower aspect ratio than for domains oriented with $\vec{b}$ parallel to the steps.

When tetracene films are grown on the high step-density, 0.3°-miscut substrate, the effect on the sub-domain anisotropy is much more pronounced. Figure 5.14b presents a TSM image of a 4ML tetracene film grown on such a high step-density substrate. Similar to the low step-density case, domains are less disordered and have a higher aspect ratio when $\vec{b}$ is parallel to the substrate steps, than when it is perpendicular to the steps. However, on comparing the “$\vec{b} \parallel$ steps” domains between the two substrates, the elongation is much more pronounced for the high step-density case (figure 5.14b) than in the low step-density case (figure 5.14a). On the other hand, no obvious difference exists between the two substrates for the “$\vec{b} \perp$ steps” domains.

**Step Influence on Major Domain Size**

While a higher step density has a significant effect on the sub-domains discussed in this chapter, and on the single-crystal domains discussed in chapter 4, they have no obvious influence over the major domains. Figure 5.15 presents typical large-scale TSM images of tetracene films grown on low step-density (0.03°-miscut) and high
Figure 5.14: TSM image demonstrating the effect of substrate steps on sub-domain shape anisotropy. a) 4ML tetracene film grown on a low step-density, 0.03°-miscut substrate, and; b) a high step-density, 0.3°-miscut substrate. On the high step-density substrate, the elongation of sub-domains that are parallel to the steps is much more pronounced than for the low step-density substrate. On the other hand, no obvious difference exists for domains oriented perpendicular to the steps.
Figure 5.15: Comparison of major domains in TSM images of 4ML films grown on low step-density (left) and high step-density (right) substrates. No apparent differences exist in the shapes or sizes of the major domains that grow on each substrate.
step-density (0.3°-miscut) substrates. While the domain sizes can vary from place to place within a film, there are no obvious systematic differences in the shapes or sizes of the domains grown on each substrate. Presumably, the molecular interaction which is responsible for the long-range continuity of the large domains is too strong to be disrupted by the presence of the substrate steps.

5.5 Chapter Summary

In this chapter it was demonstrated that lateral force microscopy (LFM) could be used to image the domain structure of the tetracene films. Two types of domains were identified:

The first domain type, called “major domains”, are on the order of tens of microns in size, and are only visible in the TSM images. They appear dominantly in two shades which correspond to the two orthogonal lattice orientations that were detected in the GIXD data from chapter 4. The lattice orientation of the major domains determines the orientation of top surface islands, demonstrating the link between island growth direction and lattice orientation.

The major domains are sub-divided into smaller domains of the second type, called “sub-domains”. The sub-domains range in size from 0.1-5µm, and are visible in both TSM and FFM images. Each major domain contains sub-domains of a uniform direction of elongation, which corresponds to the crystal surface of highest binding energy (i.e. the \( \vec{b} \) axis). It was argued that the sub-domain contrast is related to the molecular tilt direction.

The effect of substrate steps on the domains was also studied. The steps are able to induce boundaries in the sub-domains, as was the case with the single-crystal
domain boundaries discussed in chapter 4. However, the steps have no apparent effect on the major domains.
Chapter 6

Conclusion

6.1 Summary of Results

This thesis presented a detailed characterization of the various domain structures of tetracene films grown on silicon(001)-monohydride surfaces. Using grazing-incidence X-ray diffraction (GIXD) and lateral force microscopy (LFM), information pertaining to the film structure and domain size and shape distribution were obtained, and the influence of the substrate over film structure was studied. The results provide insight into the different types of domain boundaries that can exist in organic thin films, and the factors which affect them, which may assist in research efforts aimed toward understanding and optimizing charge transport in organic films.

GIXD was used to study tetracene films grown on substrates with an average step spacing of 0.26µm. Results show that the film takes on a lattice structure that is similar to bulk tetracene (a=7.70Å, b=5.93Å, and γ=90.0° for the thin-films studied here, compared to a=7.84Å, b=6.06Å, and γ=85.79° for the bulk phase), and that the silicon surface constrains the film lattice to two dominant orientations,
with the $\vec{b}$ axis aligned along the substrate (110) or (1T0) directions (i.e. parallel or perpendicular to the silicon dimer rows). Along the film $\vec{a}$ direction, the film lattice matches the periodicity of the silicon substrate (7.68Å) to within experimental uncertainty, demonstrating that a partially-commensurate relationship exists.

From an analysis of the two-dimensional profiles of the diffraction peaks, the size and anisotropy of the single-crystal domains which comprised the film were studied. Domain sizes range from about 0.05-0.2µm, depending on the film thickness and direction along which the length is measured. The domains show a maximum size when the film is 4 monolayers thick. The domains tend to be longer along the $\vec{b}$ direction than along $\vec{a}$ by about a factor of two, indicating that the preferred growth direction is along $\vec{b}$, which agrees with our expectation from surface energetics. It is also found that the top surface islands are about two orders of magnitude larger than the single-crystal domains, indicating that the islands are polycrystalline.

In order to study the effect of substrate steps on the film structure, films were grown on vicinal substrates in which the substrate step spacing is reduced to 0.026µm. The lattice parameters are unaffected by a high step-density, indicating that the lattice structure remains the same. However, the steps have the effect of inducing single-crystal domain boundaries, thereby reducing the effective single-crystal domain sizes.

LFM was used to obtain real-space information on the film domain structure. LFM images reveal the existence of two types of domains. The larger of the two (i.e. the “major domains”) correspond to regions of uniform lattice orientation, and appear in two shades in the images, corresponding to the two lattice orientations detected in the GIXD data. The major domains are on the order of tens of microns in size. This
is two orders of magnitude larger than the single-crystal domains, indicating that
the major domains are polycrystalline, containing many single-crystals which possess
the same lattice orientation, but are incoherently registered. The major domains are
divided into domains of the second type (i.e. the “sub-domains”). The sub-domains
are argued to be related to regions of uniform molecular tilt azimuth. Similar to
the single-crystal domains, the sub-domains show a preference for growth along the $\vec{b}$
axis. However, the sub-domains are larger than the single-crystal domains by up to
a factor of ten, indicating that they are also polycrystalline.

LFM was also used to study the effect of substrate steps on the domains. The steps
induce boundaries in the sub-domains in the same way as they do for the single-crystal
domains. However, they have no apparent effect on the major domain boundaries.

6.2 Future Work

In this thesis, we have presented techniques for studying the domain structure of
organic films, and have shown the existence of a few different types of domain bound-
daries. As described in section 1.1, domain boundaries are known to inhibit charge
transport in thin films, and are a fundamental reason why the carrier mobility of
thin films are lower than in single-crystals. It is our hope that the findings here re-
arding the nature of the domain structure and distribution will point out possible
directions for future theoretical and experimental work, which may lead to a better
understanding of charge transport in thin films.

Experimentally, we may carry out more work to study the link between the
domain distribution and transport properties. Two potential avenues are readily
available for this objective: The first is by use of current-sensing atomic force mi-
croscopy (CSAFM), in which a current may be passed through the film between an electrode and the AFM tip during imaging. The microscope used in the present work is equipped for this imaging mode. This method may allow the study of the dependence of transport properties on transport direction and on domain boundary density. Presumably, transport along the substrate step direction may be better than that perpendicular to the steps due to the longer domain size along that direction. Furthermore, if precise placement of the electrode is possible, the transport properties of a single domain may be determined. The second avenue is by fabrication of thin film transistors, which has previously been carried out in our lab, and successfully used for carrier mobility measurements [106]. Similar to CSAFM, this method may be used to study the dependence of transport properties on domain size and film orientation.

This research also showed that lattice orientation can be controlled to some extent by suitable substrate selection. This is of practical interest since charge transport in organic materials is anisotropic. Therefore, constraining the lattice orientation to that which optimizes mobility may help to enhance charge transport. On the silicon substrates used here, there exist two types of orthogonally oriented terraces, which resulted in two lattice orientations for our films. We have shown that the major domains, which contain crystallites of uniform lattice orientation, can span many substrate terraces. This means that each film lattice orientation may exist on either substrate terrace. However, it is unclear whether only one or both film lattice orientations may nucleate on a particular substrate terrace at the time of initial island nucleation. This question may be addressed by carrying out film growth experiments on a substrate for which only one terrace orientation exists. Such a substrate may
be produced by applying a mechanical strain to the substrate while heating [130], or by selecting a vicinal substrate with a sufficiently high miscut-angle [131]. If the film lattice orientation is, in fact, constrained by the substrate terrace orientation at the site of nucleation, then such an experiment would result in a film of a single major domain (i.e. a single lattice orientation).

Finally, as we have now demonstrated the ability to detect various types of domains, numerous opportunities emerge to study the effect of various film growth parameters (e.g., substrate temperature, deposition rate, thickness) on the domain structure. Such parameters have been extensively studied in past literature in order to determine the effect on film morphology and growth mode in various systems. An understanding of the effects of these parameters on domain structure would advance our understanding of the factors that affect film growth and quality, and may point the way toward strategies and methods for optimizing film quality for device performance.
Bibliography


163


Appendix A

X-Ray Diffraction: Background and Theory

X-ray diffraction can reveal a wealth of information pertaining to the structure of a material. In the experiments presented in this thesis, it is used to characterize the lattice structure of thin crystalline films, as well as to reveal information on preferred lattice orientation with respect to the substrate, and preferred growth directions for the single-crystal domains that comprise the film.

In order to provide a convenient reference, this chapter presents a review of the elements of diffraction theory that are necessary to understand the experimental results presented in this thesis. For a more complete reference, see Als-Nielsen and McMorrow [97]. Section A.1 details the background of conventional X-ray diffraction, while section A.2 shows how these concepts are applied to the special case of diffraction from a thin film.
A.1 Overview of X-Ray Diffraction Theory

The phenomenon of X-ray diffraction results from the scattering and resulting interference of X-rays from electrons within a material. In this section, it is shown how this interference can result in Bragg Peaks, that is, the concentration of scattered radiation into discrete directions.

It is important to note that, for the purposes of X-ray diffraction, we are primarily interested in elastically scattered photons (i.e. photons which maintain their energy and wavelength after scattering), which scatter coherently (i.e. there is a well-defined phase relationship between the incident and scattered photons). This is because the structural information that can be obtained from X-ray diffraction arises due to the appearance of diffraction peaks, which are a result of the interference of coherently scattered waves. No such interference can occur for incoherent waves (see section D of reference [132]), since the phase of the scattered photons is random. Incoherently scattered photons will result in a slowly-varying background in the measured intensity. For this reason, we will restrict the discussion to elastic X-ray scattering, and hence we will assume that the incident and reflected wavelengths are identical.

A.1.1 Diffraction from Two Scattering Points

A crystal is, by definition, a periodic material composed of a repeating pattern of some fundamental unit cell. In order to calculate the total scattered amplitude of X-rays from a macroscopic crystal, we must add the scattered amplitudes from each individual unit cell within the crystal. We therefore start by considering the interference of scattered X-rays from two spatially separated unit cells.

Figure A.1 schematically depicts the scattering of an incident wave by two unit
cells, numbered 1 and 2 in the figure, with incident and scattered wavevectors $\vec{k}$ and $\vec{k}'$. Scattered waves radiate spherically from each point, and we are interested in the phase difference between the two waves at points 1’ and 2’, at which the two scattered wavevectors are parallel.

The figure demonstrates that the separation of the two points results in a phase difference between the two scattered waves. The wavefront at point 2’ has travelled a distance of $\frac{(\vec{k}' - \vec{k}) \cdot \vec{r}}{k}$ farther than that at 1’. Therefore, the phase of the wavefront from point 2 will be shifted ahead of that from point 1 by an amount;

$$\phi = -(\vec{k}' - \vec{k}) \cdot \vec{r} = -\vec{Q} \cdot \vec{r}.$$  \hspace{1cm} (A.1)

Here, $\vec{Q} = \vec{k}' - \vec{k}$ is known as the scattering vector, or momentum transfer vector. We therefore know that, when adding amplitudes from spherical waves scattered from two separate points, we must apply the following phase factor to each scattered amplitude:

$$e^{i\phi} = e^{-i\vec{Q} \cdot \vec{r}}$$ \hspace{1cm} (A.2)

where $\vec{r}$ is the position of the scattering point with respect to some common origin.

**A.1.2 Diffraction from a Crystal**

The total scattering amplitude from a crystal, which is composed of a periodic lattice of scattering points, may be easily derived using the ideas of the last section. Consider a collection of $N$ unit cells, each assigned a position vector $\vec{R}_n$, and each with scattering amplitude $F_n(\vec{Q})$. The scattering amplitudes $F_n(\vec{Q})$ are known as the structure factor of the unit cell (It will later be shown that the structure factor,
Figure A.1: The geometry of the scattering process from two scattering points: An incident wave of wavevector $\vec{k}$ is scattered from two spatially separated points. The outgoing wave has wavevector $\vec{k'}$, which is equal in magnitude to $\vec{k}$. The outgoing waves will differ in phase as a result of the spacial separation of the scattering points.
like the phase factor derived in section A.1.1, only depends on $\vec{Q}$, and not on the
individual wavevectors $\vec{k}$ and $\vec{k}'$). The total scattering amplitude from the collection
of unit cells is simply the sum of the amplitude contribution from each unit cell:

$$S(\vec{Q}) \propto \sum_n F_n(\vec{Q}) \cdot e^{-i\vec{Q} \cdot \vec{R}_n}. \quad (A.3)$$

The proportionality sign is used since the actual scattering amplitude depends on
other factors, including incident wave polarization, as explained in section A.1.4.

In a crystal, the unit cells are identical, and therefore have the same scattering
amplitude $F(\vec{Q})$. Furthermore, the position of each cell can be written as $\vec{R}_n =
n_a \vec{a} + n_b \vec{b} + n_c \vec{c}$, where the coefficients $n_i$ are integers, and the vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$ are
linearly-independent primitive lattice vectors, which point from one unit cell to an
identical position in an adjacent unit cell. Thus for a crystal, equation A.3 can be
rewritten as:

$$S(\vec{Q}) \propto F(\vec{Q}) \sum_{n_a,n_b,n_c} e^{-i\vec{Q} \cdot (n_a \vec{a} + n_b \vec{b} + n_c \vec{c})}
\propto F(\vec{Q}) \sum_{n_a=1}^{N_a} \left( e^{-i\vec{Q} \cdot \vec{a}} \right)^{n_a}
\sum_{n_b=1}^{N_b} \left( e^{-i\vec{Q} \cdot \vec{b}} \right)^{n_b}
\sum_{n_c=1}^{N_c} \left( e^{-i\vec{Q} \cdot \vec{c}} \right)^{n_c}. \quad (A.4)$$

In the limit where there is a very large number of crystallites $N$, it can be seen
from equation A.4 that a non-zero amplitude can only occur if the exponents are an
integer multiple of $2\pi$. In this case, the total amplitude will just be $F(\vec{Q}) \cdot N$, where $N = N_a \cdot N_b \cdot N_c$, the total number of cells. In any other case, the phase factor will
have an average value of zero over all the terms in the sum.

This shows that, for a crystal containing a large number of unit cells, only partic-
ular values of the scattering vector $\vec{Q}$ will yield non-zero scattered intensities. These
values of $\vec{Q}$ must satisfy the following conditions:

$$\vec{Q} \cdot \vec{a} = 2\pi \cdot \text{integer}$$
$$\vec{Q} \cdot \vec{b} = 2\pi \cdot \text{integer}$$
$$\vec{Q} \cdot \vec{c} = 2\pi \cdot \text{integer}$$ 

(A.5)

To further interpret this condition, without loss of generality, we can decompose $\vec{Q}$ into three (not necessarily orthogonal) components, $\vec{a}^*$, $\vec{b}^*$, and $\vec{c}^*$, such that $\vec{a}^*$ is perpendicular to $\vec{b}$ and $\vec{c}$, $\vec{b}^*$ is perpendicular to $\vec{a}$ and $\vec{c}$, and $\vec{c}^*$ is perpendicular to $\vec{a}$ and $\vec{b}$.

$$\vec{Q} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*.$$ 

(A.6)

The conditions on $\vec{Q}$ then break down into three conditions on $h$, $k$, and $l$:

$$h\vec{a}^* \cdot \vec{a} = 2\pi \cdot \text{integer}$$
$$k\vec{b}^* \cdot \vec{b} = 2\pi \cdot \text{integer}$$
$$l\vec{c}^* \cdot \vec{c} = 2\pi \cdot \text{integer}$$ 

(A.7)

For convenience, the vectors $\vec{a}^*$, $\vec{b}^*$, and $\vec{c}^*$ may be defined such that $\vec{a}^* \cdot \vec{a} = 2\pi$, $\vec{b}^* \cdot \vec{b} = 2\pi$, and $\vec{c}^* \cdot \vec{c} = 2\pi$. In this case, the conditions in A.7 are satisfied under the very simple condition that $h$, $k$, and $l$ are integers.
A.1.3 The Reciprocal Lattice

In the last section it was shown that, in the case of X-ray diffraction from a crystal containing a large number of unit cells, a non-zero intensity may only be measured if \( \mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \), where \( h, k, \) and \( l \) are integers, and the vectors \( \mathbf{a}^*, \mathbf{b}^*, \) and \( \mathbf{c}^* \) satisfy some simple conditions. These conditions are such that the vector \( \mathbf{a}^* \) is perpendicular to both \( \mathbf{b} \) and \( \mathbf{c} \), and that \( \mathbf{a}^* \cdot \mathbf{a} = 2\pi \) (plus cyclic permutations of these conditions). In order to ensure that these conditions are satisfied, \( \mathbf{a}^*, \mathbf{b}^*, \) and \( \mathbf{c}^* \) are defined as follows:

\[
\begin{align*}
\mathbf{a}^* &= 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \\
\mathbf{b}^* &= 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot (\mathbf{c} \times \mathbf{a})} \\
\mathbf{c}^* &= 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})}
\end{align*}
\] (A.8)

These vectors are known as the Reciprocal Lattice Basis Vectors. In the limit of a crystal with a large number of unit cells \( N \), a non-zero diffracted intensity can occur where \( \mathbf{Q} \) is an integer combination of these basis vectors. Such a value of \( \mathbf{Q} \) is known as a Reciprocal Lattice Vector, and the set of all reciprocal lattice vectors is simply called the reciprocal lattice.

To aid in interpreting the meaning of the reciprocal lattice vectors, consider a crystal with a rectangular lattice, as shown in figure A.2. The lattice vectors for this crystal are given by \( \mathbf{a} = (a, 0, 0) \), \( \mathbf{b} = (0, b, 0) \), and \( \mathbf{c} = (0, 0, c) \). According to A.8, the reciprocal lattice vectors will be given by \( \mathbf{a}^* = \left( \frac{2\pi}{a}, 0, 0 \right) \), \( \mathbf{b}^* = \left( 0, \frac{2\pi}{b}, 0 \right) \), and \( \mathbf{c}^* = \left( 0, 0, \frac{2\pi}{c} \right) \). Notice that the reciprocal lattice vector \( \mathbf{a}^* \) is perpendicular to the set of lattice planes with Miller indices 100, and has a magnitude of \( \frac{2\pi}{a} \), which is equal to...
\( \frac{2\pi}{d_{100}} \) (\( d_{100} \) being the distance between these planes). Similarly, the reciprocal lattice vector \( \vec{a}^* + \vec{b}^* \) is perpendicular to the set of planes with Miller indices 110, and can be shown to have a magnitude equal to \( \frac{2\pi}{d_{110}} \). Indeed, it can be generally shown that, for any crystal, the reciprocal lattice vector \( h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \) is perpendicular to a set of lattice planes with miller indices \( hkl \), and the shortest such reciprocal lattice vector which is parallel to \( h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \) will have a magnitude of \( \frac{2\pi}{d_{hkl}} \).

Finally, with the definition of the reciprocal lattice established in this section, we may use equation A.4 to calculate the total scattered intensity from a crystal under the condition that \( \vec{Q} \) corresponds with a reciprocal lattice vector \( \vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \).

We have:

\[
I_{\text{crystal}}(\vec{G}_{hkl}) \propto |S(\vec{G}_{hkl})|^2
\]

\[
\propto \left| F(\vec{G}_{hkl}) \sum_{n_a=1}^{N_a} (e^{-i\vec{h} \cdot \vec{a}}) \sum_{n_b=1}^{N_b} (e^{-i\vec{k} \cdot \vec{b}}) \sum_{n_c=1}^{N_c} (e^{-i\vec{l} \cdot \vec{c}}) \right|^2
\]

\[
\propto \left| F(\vec{G}_{hkl}) \sum_{n_a=1}^{N_a} (e^{-i2\pi h}) \sum_{n_b=1}^{N_b} (e^{-i2\pi k}) \sum_{n_c=1}^{N_c} (e^{-i2\pi l}) \right|^2
\]

\[
\propto \left| F(\vec{G}_{hkl}) \sum_{n_a=1}^{N_a} \sum_{n_b=1}^{N_b} \sum_{n_c=1}^{N_c} 1 \right|^2
\]

\[
I_{\text{crystal}}(\vec{G}_{hkl}) \propto N^2 \cdot |F(\vec{G}_{hkl})|^2
\]

(A.9)

Therefore, the total scattered intensity is proportional to the square of the number of unit cells in the crystal, and the squared magnitude of the structure factor.
Figure A.2: A rectangular crystal lattice. Only the a-b plane is shown for clarity. The distances $d_{hkl}$ between two particular crystal planes are indicated.
A.1.4 The Structure Factor and Atomic Form Factor

The structure factor $F(\vec{Q})$ was introduced in section A.1.2, and is defined as the scattering amplitude of a single crystal unit-cell for a particular scattering vector $\vec{Q}$. In this section, it is shown how the structure factor is calculated. The atomic form factor $f(\vec{Q})$ will arise as a part of the discussion, and is similarly defined as the scattering amplitude from a single atom.

X-ray diffraction from a crystal, at the fundamental level, is a result of photons scattering from individual electrons within the crystal. Classically, the scattered light can be thought of as the radiated field from an accelerating electron, with its acceleration arising due to the force produced by the oscillating electric field of an incident wave.

Consider the scenario shown in figure A.3, in which an X-ray beam with a polarization along the z-axis (and hence, a direction of propagation within the x-y plane), and amplitude $E_{\text{in}}$, is incident upon a free electron (the more realistic case of a bound electron will be discussed later). The amplitude of the radiated field $E_{\text{rad}}$ from the electron, as measured at a large distance away (as compared with the full range of motion of the electron) is given by the following:

$$E_{\text{rad}} = -\frac{e^2}{4\pi\varepsilon_0 m_e c^2} \cdot \frac{1}{r} \cdot e^{-i kr} \cdot \cos(\psi) \cdot E_{\text{in}}$$

$$= -\frac{r_0}{r} \cdot e^{-i kr} \cdot \cos(\psi) \cdot E_{\text{in}} \quad (A.10)$$

The derivation of A.10 can be found in appendix B of reference [97]. The angle $\psi$ is the angle between the position vector $\vec{r}$ (i.e. the point at which we are measuring the radiated field) and the x-y plane (i.e. the plane perpendicular to the incident
Figure A.3: Scattering of light from a single electron at the origin. A portion of the incident wave proceeds, unscattered, in the original direction of incidence with amplitude $\vec{E}_{in}$. The induced acceleration of the electron produces a spherical wave propagating radially with amplitude $\vec{E}_{rad}$. 
beam polarization) The constant $r_0$, known as the *Thomson Scattering Length*, has also been introduced, and is defined as:

$$r_0 = \frac{e^2}{4\pi\epsilon_0 m_e c^2}. \quad (A.11)$$

The radiated field propagates radially from the electron as a spherical wave. The negative sign in A.10 signifies a phase shift of 180° with respect to the incident wave. That is, the component of the radiated field that is parallel to the incident beam polarization vector will be inverted with respect to the incident beam. The component of the radiated field which lies in the x-y plane will be in the radial direction. Notice that, due to the $\cos(\psi)$ factor, the scattering amplitude is highest within the plane that is perpendicular to the incident beam polarization. This is important to consider when designing an experiment with a polarized X-ray source, such as that of a synchrotron.

Note that the radiated field in equation A.10 is inversely proportional to the electron mass $m_e$. Therefore if we performed the same analysis for the scattered amplitude from a proton, we would find that the radiated field would be much smaller, and can thus be neglected in materials containing an equal number of protons and electrons.

For X-ray scattering from two or more electrons, we can simply apply a phase shift, as we have in the preceding sections, to account for the spatial separation of the electrons. Making use of equation A.1, the phase difference between coherent waves scattered by two electrons separated by vector $\vec{r}$ is just $-\vec{Q} \cdot \vec{r}$. Therefore, when X-rays are scattered coherently from a system of many electrons, as in an atom, the contribution of electron $m$ (located at position $\vec{r}_m$) to the total scattered amplitude,
measured a distance \( r \) away from the system of electrons, is;

\[
E_{rad,n} = -E_{in} \cdot \frac{e^{-ikr}}{r} \cdot \cos(\psi) \cdot r_0 \cdot e^{-iQ \cdot \vec{r}_m}.
\] (A.12)

This equation is valid if \( r \) is much larger than the system of electrons. From this, the total radiated intensity measured from a system of \( Z \) electrons at a distance \( r \) away is;

\[
E_{rad,\text{total}} = E_{in} \cdot \frac{e^{-ikr}}{r} \cdot \cos(\psi) \cdot \sum_{m=1}^{Z} \left( -r_0 \cdot e^{-iQ \cdot \vec{r}_m} \right).
\] (A.13)

We now extend this idea to a system of electrons confined to an atom. When these electrons are in atomic orbitals, they can be regarded as a spatial electron distribution with an electron density of \( \rho(\vec{r}) = |\psi(\vec{r})|^2 \), where \( \psi(\vec{r}) \) is the orbital wavefunction. In this picture, the above sum can be turned into an integral, and the total radiated amplitude from an atom can be written as;

\[
E_{rad,\text{atom}} = E_{in} \cdot \frac{e^{-ikr}}{r} \cdot \cos(\psi) \cdot \int d\vec{r} \left( -r_0 \cdot e^{-iQ \cdot \vec{r}} \cdot \rho(\vec{r}) \right).
\] (A.14)

where \( \rho(\vec{r}) \) represents the total electron density at point \( \vec{r} \) within the atom.

The concept of the atomic form factor \( f_0(\vec{Q}) \) arises naturally from equation A.14. We define;

\[
f_0(\vec{Q}) = \int d\vec{r} \cdot e^{-iQ \cdot \vec{r}} \cdot \rho(\vec{r})
\] (A.15)
Then the total scattering amplitude from an atom is:

\[
E_{\text{rad,atom}} = E_{\text{in}} \cdot e^{-i k r} \cdot \cos(\psi) \cdot \left( -r_0 \cdot f_0(\vec{Q}) \right) \tag{A.16}
\]

Equation A.16 was derived under the assumption that the electron is a free distribution of charge, in the sense that its scattering properties will not be affected by the fact that it is energetically bound to an atom. In reality, this binding effect will result in a small correction to the atomic form factor, and will be discussed in section A.1.5.

Since a crystal unit-cell is a collection of atoms, the concept of a unit-cell structure factor is a simple extension of the atomic form factor. The scattering amplitude for a single unit cell, measured a large distance \( r \) away, can be found by adding the contributions, given by equation A.16, from each atom within the unit cell. This leads to the following equation:

\[
E_{\text{rad,cell}} = E_{\text{in}} \cdot e^{-i k r} \cdot \cos(\psi) \cdot \left( -r_0 \cdot \sum_n f_{0,n}(\vec{Q}) \cdot e^{-i\vec{Q} \cdot \vec{r}_n} \right)
\]

\[
= -E_{\text{in}} \cdot \frac{r_0}{r} \cdot e^{-i k r} \cdot \cos(\psi) \cdot F_{\text{cell}}(\vec{Q}) \tag{A.17}
\]

The sum is taken over all atoms in the cell, and \( f_{0,n}(\vec{Q}) \) and \( \vec{r}_n \) are, respectively, the atomic form factor and position of atom \( n \). In this equation, the unit-cell structure factor was naturally defined as:

\[
F_{\text{cell}}(\vec{Q}) = \sum_n f_{0,n}(\vec{Q}) \cdot e^{-i\vec{Q} \cdot \vec{r}_n} \tag{A.18}
\]
The Bias toward Forward Scattering

It is important to note that the atomic form factor introduces a bias toward forward scattering ($\vec{Q} = 0$), especially at very high X-ray energies. Clearly, in the limit of $\vec{Q} \to 0$, the form factor in equation A.15 simply equates to the total number of electrons $Z$ in the atom. Whereas if $\vec{Q} \to \infty$, then the factor $e^{-i\vec{Q} \cdot \vec{r}}$ will fluctuate very rapidly around the unit circle on the complex plane, causing positive and negative real and imaginary numbers to cancel each other out within each volume element in the integral, and the form factor will tend toward zero.

As a simple, specific example, we will calculate the form factor for an electron in the 1s state of hydrogen. The form factor is given by the following integral, taken over all space:

$$f_{1s}(\vec{Q}) = \int d\vec{r} \cdot \psi_{1s}^2(\vec{r}) \cdot e^{-i\vec{Q} \cdot \vec{r}}$$

$$= \int d\vec{r} \cdot \frac{1}{\pi a_0^2} \cdot e^{-2r/a_0} \cdot e^{-i\vec{Q} \cdot \vec{r}}$$

$$= \int_0^\infty r^2 dr \int_0^\pi \sin(\rho) d\rho \int_0^{2\pi} d\phi \cdot \frac{1}{\pi a_0^3} \cdot e^{-2r/a_0} \cdot e^{-iQr \cos(\rho)}$$

$$= \frac{1}{\left(\left(\frac{Qa_0}{2}\right)^2 + 1\right)^2}$$  \hspace{1cm} (A.19)

Here, $Q$ is the magnitude of the scattering vector $\vec{Q}$, which can be written in terms of the wavevector $k$ as $Q = 2k \sin(\theta)$, where $\theta$ is the Bragg angle (i.e. half the angle between the incident and scattered wavevectors). Making this substitution leads to:

$$f_{1s}(\theta) = \frac{1}{\left(\left(\frac{2kao \sin(\theta)}{2}\right)^2 + 1\right)^2}$$  \hspace{1cm} (A.20)

182
The resulting function of $f_{1s}(\theta)$ is plotted versus $\theta$ in figure A.4. For the purposes of the plot, $k a_0$ is given a numerical value of 2.68, which corresponds to the wavelength used in the experiments described in this thesis. The highest scattering amplitude occurs for small scattering angles, whereas the amplitude will drop to zero when $\theta = 90^\circ$ (which corresponds to scattering in the direction opposite the incident beam).

This is an important consideration in diffraction experiments. Higher order diffraction peaks (i.e. peaks that reside at larger values of $Q$) will naturally be lower in intensity as a result of this orientational dependence of the atomic form factor. Therefore the lower order peaks are most easily detected.

### A.1.5 The Scattering Cross-Section

The total scattering cross-section $\sigma$ for a scattering object (such as an atom) is defined as the ratio of the total rate of scattered photons to the incident photon flux. Conceptually, it can be thought of as the effective cross-sectional area of the atom if we imagine it as a sphere which scatters any photon that strikes it, as depicted in figure A.5. With this intuitive picture in mind, for an electron situated in an incident beam with intensity $I_{in}$ (for the purposes in this thesis, $I$ will be defined as the photon flux rate), the rate at which photons are scattered (i.e. the number $N_{sc}$ of photons scattered in differential time interval $dt$) is;

$$\frac{dN_{sc}}{dt} = \sigma \cdot I_{in}. \quad (A.21)$$

This conceptual picture thus corresponds to the mathematical definition of the cross section.
Figure A.4: A numerical plot of the dependence of the atomic form factor $f(\vec{Q})$ on the Bragg angle $\theta$ for the 1s state of a hydrogen atom. A wavelength of 1.24Å was used for the plot. Note that a Bragg angle of 90° corresponds to X-rays scattering in the direction opposite the incident X-ray beam.
Figure A.5: A conceptual model for the definition of the electron cross-section for X-ray scattering. The electron is modelled as a spherical scattering object, which blocks an area of the beam equal to the cross section $\sigma$. With a flux $I_{in}$ of incident photons (black arrows), the rate at which scattered photons (red arrows) are produced is easily seen to be given by equation A.21.
Similarly, the differential cross-section \( \frac{d\sigma}{d\Omega} \) tells us the effective cross-section for scattering into a particular solid angle \( d\Omega \). The rate at which electrons are scattered, per unit solid angle, is then;

\[
\left( \frac{dN_{sc,d\Omega}}{dt} \right) / d\Omega = \left( \frac{d\sigma}{d\Omega} \right) \cdot I_{in}.
\]  

(A.22)

At a distance of \( r \) away from the electron, the solid angle \( d\Omega \) spans an area of \( r^2 d\Omega \). Therefore the total rate at which photons are scattered through a solid angle \( d\Omega \) is;

\[
\frac{dN_{sc,d\Omega}}{dt} = I_{sc} \cdot r^2 d\Omega
\]

(A.23)

where \( I_{sc} \) is the scattered intensity through \( d\Omega \), defined as number of scattered photons per second per unit area.

Combining equations A.22 and A.23, we have the following relation between the incident and scattered intensities:

\[
I_{sc} = I_{in} \cdot \frac{1}{r^2} \left( \frac{d\sigma}{d\Omega} \right)
\]

(A.24)

Solving for the differential cross-section, and then inserting equation A.16, results in the following expression for the differential scattering cross-section of an atom:

\[
\frac{d\sigma}{d\Omega} = r^2 \frac{I_{sc}}{I_{in}}
= r^2 \frac{|E_{rad}|^2}{|E_{in}|^2}
= \cos^2(\psi) \cdot r_0^2 \cdot |f_0(\vec{Q})|^2
\]

(A.25)
Note that both the $\cos^2(\psi)$ and $|f_0(\mathbf{Q})|^2$ factors depend on the scattering vector $\mathbf{Q}$. Recall that $\psi$ is the angle between the scattered wavevector $\mathbf{k}'$ and the plane which is perpendicular to the incident beam polarization (i.e. the x-y plane in figure A.3).

If the atomic form factor is known, then the total cross-section can be found by integrating this expression over all angles. For example, for a single, free electron, treated as a point particle at the origin, the form factor $f_0(\mathbf{Q})$ is just 1 (this can be obtained by substituting $\rho(\mathbf{r}) = \delta(\mathbf{r})$ into equation A.15). From this, the following well-known expression for the X-ray scattering cross-section of a free electron is obtained:

$$\sigma_{\text{free electron}} = \frac{8\pi}{3} r_0^2.$$  \hspace{1cm} (A.26)

**Effect of Bound Electrons on X-ray Scattering**

Notice from equation A.25 that the differential scattering cross-section for an atom, which determines the scattered intensity through equation A.24, is proportional to the squared magnitude of the atomic form factor $f_0(\mathbf{Q})$. Recall that the form of $f_0(\mathbf{Q})$ in equation A.15 was derived under the assumption that the electrons are free, and form a continuous distribution around the atom in their atomic orbitals. In order to be completely general, some corrections need to be made to account for the fact that the electrons are actually in bound states. To do this, the atomic form factor $f_0(\mathbf{Q})$ for the case of free electrons, is replaced by the following form which takes energy corrections into account:

$$f(\mathbf{Q}, \omega) = f_0(\mathbf{Q}) + f'(\omega) + if''(\omega).$$  \hspace{1cm} (A.27)
Since the two new terms, $f'(\omega)$ and $f''(\omega)$, are a result of the electrons being energetically bound to the atom, they are assumed to only depend on the scattered photon energy $\hbar \omega$.

The correction terms in equation A.27 are known as the “dispersion corrections”, or the “anomalous scattering corrections” to the atomic form factor. The details of their calculation and measurement are not relevant to the subject matter of this thesis (for some discussion of these terms, along with some methods of calculation, see chapter 8 of reference [97]). However it is useful to note that the correction terms become negligible if the X-ray energy is high compared to the resonant absorption energies for a particular atom. This means that bound electrons have the scattering properties of free electrons at high X-ray energies.

The experiments described in this thesis are based on tetracene, which is composed of carbon and hydrogen. At the X-ray energies used in the experiments here, the dispersion corrections should be on the order of a fraction of a percent of the uncorrected form factor $f_0(\vec{Q})$ [133]. Therefore, the discussion with respect to free electrons thus far should practically apply to our tetracene films.

### A.2 Diffraction from a Thin Film

#### A.2.1 Crystal Truncation Rods

The reciprocal-space diffraction pattern (i.e. the scattered intensity as a function of $\vec{Q}$) for a thin crystalline film is different from that of a three-dimensional crystal in that rods will be formed in reciprocal-space, as opposed to discrete points. In this section, it will be shown how these features, known as crystal truncation rods are
formed. This feature of the diffraction pattern is an important consideration for thin film GIXD experiments such as those presented in this thesis.

We start by applying equation A.4, which describes the scattering amplitude for a general three-dimensional crystal, to the case of a thin crystalline film, and again express $\vec{Q}$ as a linear combination of the reciprocal-lattice basis vectors:

$$\vec{Q} = \frac{Q_a^*}{a^*} \vec{a}^* + \frac{Q_b^*}{b^*} \vec{b}^* + \frac{Q_c^*}{c^*} \vec{c}^*$$ (A.28)

Then, in the limit of a very large number of unit cells in the a-b plane ($N_{ab} = N_a \cdot N_b$), the sums of complex exponentials become sums of delta functions, and equation A.4 becomes;

$$S(\vec{Q}) = F(\vec{Q}) \sum_{n_a=1}^{N_a} \left(e^{-i2\pi \frac{Q_a^*}{a^*} n_a}\right) \sum_{n_b=1}^{N_b} \left(e^{-i2\pi \frac{Q_b^*}{b^*} n_b}\right) \sum_{n_c=1}^{N_c} \left(e^{-i2\pi \frac{Q_c^*}{c^*} n_c}\right)$$

$$= F(\vec{Q}) \left(\sum_{h=-\infty}^{\infty} \delta \left(\frac{Q_a^*}{a^*} - h\right)\right) \left(\sum_{k=-\infty}^{\infty} \delta \left(\frac{Q_b^*}{b^*} - k\right)\right) \sum_{n_c=1}^{N_c} \left(e^{-i2\pi \frac{Q_c^*}{c^*} n_c}\right)$$

Equation A.29 demonstrates how crystal truncation rods are formed. The delta functions in the bracketed sums indicate that a measurable intensity can only be obtained if $\frac{Q_a^*}{a^*}$ and $\frac{Q_b^*}{b^*}$ are integers. However this does not apply to the third sum over $n_c$ since only a finite number of unit cells exist in the $\vec{c}^*$ direction, and therefore the sum cannot be replaced by a sum of delta functions.

To interpret this more specifically, note that a general reciprocal lattice vector can be written as $\vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$, where $h$, $k$, and $l$ are integers. Since $\vec{c}^*$ is perpendicular to the a-b plane, the family of $hkl$ reciprocal lattice points with $h$
and \( k \) fixed, and \( l \) varying, will form a vertical column, all with a common point of projection onto the a-b plane. Each such column can be given a simplified index of the form \( hk \). If the crystal is thin along the \( \vec{c}^* \) direction, then the column will not be composed of discrete points, but will instead have some continuous structure which is defined by the unbracketed sum in A.29.

When this continuous structure exists in the columns of reciprocal lattice points that are perpendicular to the a-b plane, they become what are called *crystal truncation rods* because they result from the fact that the crystal is truncated along this direction. The intensity profiles of the rods for a few different crystal thicknesses, calculated numerically from the unbracketed sum in equation A.29, are shown in figure A.6.

### A.2.2 The Index of Refraction for X-rays

The critical angle for total external reflection, which will later be introduced, results in important considerations for optimizing surface sensitivity in GIXD experiments. Before this concept can be discussed, we must first introduce the index of refraction for X-rays passing through a material.

It is first shown how the index of refraction, as classically defined in optics, arises from a scattering description of the refraction process. Imagine that a planar X-ray beam is incident on a thin layer of free electrons, as depicted in figure A.7. The layer thickness \( t \) is small enough that multiple scattering and absorption can be ignored (i.e. all scattering points in the layer receive the same incident intensity). The total beam intensity is measured at point ‘\( P \)’, which is located a distance \( d \) from the other side of the layer, and such that \( d \) is much larger than the X-ray wavelength.
Figure A.6: Schematic illustration of the reciprocal-space diffraction pattern for a thin, two-dimensional crystal, which is only a small number $N_c$ of unit cells thick along the $\vec{c}$ direction. a) $N_c = 1$, b) $N_c = 2$, c) $N_c = 3$, and d) $N_c = 4$. The emergence of discrete diffraction peaks from continuous crystal truncation rods is apparent as $N_c$ increases. Note that the horizontal width of the rods here represents intensity. The width does not represent the spatial width of the rod, which is infinitesimal for a large crystal.
Figure A.7: Illustration of the refraction process described in terms of scattering from every point in a layer of free electrons. The measured amplitude at point ‘P’ is the sum of contributions from all scattering points ‘Q’ in the layer, and the incident beam that passes through the layer unscattered. The origin is denoted by ‘0’. The incident wavefront is represented by the red lines.
The total measured field amplitude at point ‘P’ will be the sum of contributions from all scattering points ‘Q’ within the layer, as well as the portion of the incident beam that passes through unscattered (which, in this approximation, is the entire beam). Starting with equation A.12, which describes the scattering amplitude for a single electron, the scattered amplitude from a particular point ‘Q’, which has coordinates \((x, y, z)\) and volume \(dV\), measured at point ‘P’ will be

\[
d\vec{E}_{P,\text{scatt}} = -r_0 e^{i k R} \frac{\rho}{R} \cos(\psi) E_0 e^{i k z} \rho dV \left( \frac{(-xy, x^2 + (d - z)^2, y(d - z))}{\sqrt{(xy)^2 + (x^2 + (d - z)^2)^2 + (y(d - z))^2}} \right)
\]

Here, \(\rho\) is the electron density in the layer. The bracketed term is a unit vector which satisfies the polarization conditions of the scattered wave. That is, it is perpendicular to the vector \(\vec{R} = (-x, -y, d - z)\) (i.e. the direction of propagation, which points from ‘Q’ to ‘P’), and to the magnetic field \(\vec{B}\) (which, being perpendicular to \(\vec{R}\) and \(\vec{E}_0\), is parallel to the vector \(\vec{R} \times \vec{E}_0 = (-(d - z), 0, -x)\)).

The resulting expression for the total scattered amplitude at point ‘P’, after integrating the above expression over the entire electron layer, is

\[
\vec{E}_{P,\text{scatt}} = -\frac{2\pi i}{k} \rho E_0 e^{i k d} \hat{y}.
\]

The derivation is omitted for the sake of brevity. For some approaches on how to carry out the calculation, see section 10.11 of reference [134], or section 3.2 of reference [97].

When adding this expression to the contribution from the unscattered incident
wave, the total amplitude at point 'P' is found to be

\[ \vec{E}_{P,\text{tot}} = E_0 e^{ikd} \hat{y} \left( 1 - \frac{2\pi \rho t}{k r_0} \right). \tag{A.32} \]

To relate this to the index of refraction \( n \), we again analyze the scenario of figure A.7, but this time with the view that the velocity of the X-ray wavefront changes from \( c \) to \( v = c/n \) as it passes through the electron layer. In this case the wavevector changes from \( k = \omega/c \) to \( k' = \omega/v = \omega n/c = nk \). The phase shift experienced by the wave after passing through the layer is then \( k't \), and the phase difference from the back of the layer to point ‘P’ will be \( k(d - t) \). The total field at point ‘P’ is therefore

\[ \vec{E}_P = E_0 e^{i(k't + k(d-t))} \hat{y} \]

\[ = E_0 e^{ikd} e^{ikt(\frac{n-1}{n})} \hat{y} \]

\[ \approx E_0 e^{ikd} (1 + i\pi(n - 1)) \hat{y}. \tag{A.33} \]

The approximation was taken to first order in the layer thickness \( t \). When this expression is compared with equation A.32, the following expression for \( n \) is obtained:

\[ n = 1 - \frac{2\pi \rho r_0}{k^2} \]

\[ = 1 - \delta \tag{A.34} \]

where \( \delta = 2\pi \rho r_0/k^2 \).

Equation A.34 tells us that the index of refraction of a layer of free electrons is actually less than 1. Since electrons bound in materials behave as free electrons when
responding to high-energy X-rays, as discussed in section A.1.5, the refractive index will be less than 1 for X-rays of sufficiently high energies passing through a material. This analysis and result would not apply to visible light, for which the effects of bound electrons becomes significant, and result in an index of refraction that is greater than 1.

Note that an index of refraction of less than 1 does not violate relativity, as one might initially suppose. This is because the index of refraction is defined in terms of the phase velocity $v$ of light in the medium ($n = c/v$). The calculation of $n$ above was based on a determination of the effective phase velocity of X-rays in the electron layer to produce the observed field at the observation point 'P' that arises as a result of the interference of scattered X-rays. This interference apparently results in an effective phase velocity in the electron layer which exceeds $c$, the speed of light in vacuum. However a modulated signal, or an X-ray pulse, will not travel through the layer faster than $c$, and so no information can be transmitted faster than $c$, as required by relativity.

To complete the discussion of the index of refraction, we account for absorption by adding an imaginary part $i\beta$ to the expression. Adding this term to the index $n$ in the third line of equation A.33, results in a factor of $e^{-\beta kt}$ in the final expression for $\vec{E}_P$, which represents exponential decay of the transmitted beam with layer thickness. The parameter $\beta$ therefore represents absorption by the material, and the final form of the refractive index $n$ is therefore;

$$n = 1 - \delta + i\beta.$$  \hspace{1cm} (A.35)
**A.2.3 The Critical Angle for Total External Reflection**

In the previous section, the index of refraction for X-rays was shown to be slightly less than 1. The significance of this result for \( n \) is that it leads to the existence of a critical angle \( \alpha_c \) for total external reflection of X-rays incident on a material. In this section, the expression for the critical angle is derived.

When an X-ray beam is incident on an interface between two materials, as in figure A.8, the wave is partially reflected from, and partially transmitted through the interface. The amplitude of the transmitted wave \( \vec{E}_t \) will be some complex fraction \( t \) of the incident wave \( \vec{E}_0 \). The wavevector changes from \( \vec{k} \) to \( \vec{k}_t \) as the wave crosses the interface, where the magnitudes are related by \( k_t = \frac{n_2}{n_1} k \), and the directions are related through Snell’s law which will be introduced shortly. The form of the transmitted wave is

\[
\vec{E}_t = t \cdot \vec{E}_0 \cdot e^{i \vec{k}_t \cdot \vec{r}}
\]  

(A.36)

For X-rays passing from air to a material, \( n_1 \approx 1 \) and \( n_2 = 1 - \delta + i \beta \). If \( \vec{k}_t \) is written in terms of its components which are parallel \( (k_{\parallel}) \) and perpendicular \( (k_{\perp}) \) to the interface, and the coordinates are defined as in figure A.8, then the transmitted field is as follows:

\[
\vec{E}_t = t \cdot \vec{E}_0 \cdot e^{i (k_{\parallel} x + k_{\perp} z)}
\]

\[
= t \cdot \vec{E}_0 \cdot e^{i k_t (x \cos(\alpha_t) + z \sin(\alpha_t))}
\]

\[
= t \cdot \vec{E}_0 \cdot e^{i n_2 k(x \cos(\alpha_t) + z \sin(\alpha_t))}
\]

\[
= t \cdot \vec{E}_0 \cdot e^{i n_2 k x \cos(\alpha_t)} e^{i n_2 k z \sin(\alpha_t)}
\]  

(A.37)
In order to ensure continuity of the field, the component of the wavevector that lies parallel to the interface must have the same magnitude on both sides of the interface. This results in Snell’s Law:

\[ \cos(\alpha_i) = n_2 \cos(\alpha_t) \]  \hspace{1cm} (A.38)

To apply these results to GIXD, we are interested in small incident angles. Since \( n_2 \) is very close to 1, a small incident angle \( \alpha_i \) will result in a small transmission angle \( \alpha_t \), which justifies a small-angle approximation to equation A.38:

\[ 1 - \frac{\alpha_i^2}{2} = (1 - \delta + i\beta)(1 - \frac{\alpha_t^2}{2}) \]  \hspace{1cm} (A.39)

This can be simplified to yield the following expression for the \( \alpha_t \) in terms of \( \alpha_i \):

\[ \alpha_t^2 = \alpha_i^2 - 2\delta + 2i\beta \]  \hspace{1cm} (A.40)

Here, since the angles and parameters \( \delta \) and \( \beta \) are small, only terms of second order or less were kept.

Equation A.40 demonstrates that, since the index of refraction has a small imaginary part \((i\beta)\), the transmission angle \( \alpha_t \) is also a complex number. Furthermore, since we have established that \( \alpha_t \) is small, we can apply the small-angle approximation
Figure A.8: Definition of the variables in the Fresnel Equations (A.43). A wave with wavevector $\hat{k}_i$ is incident on an interface between two mediums with refractive indices $n_1$ and $n_2$, and magnetic permeabilities $\mu_1$ and $\mu_2$, with incident angle $\alpha_i$. The wave partially reflects, and partially transmits through the interface. The angle of reflection will also be $\alpha_i$, and the angle of transmission is $\alpha_t$. 
to equation A.37 as follows:

\[
\vec{E}_t \approx t \cdot \vec{E}_0 \cdot e^{ikx} e^{ikz} e^{i(\delta\alpha t - 2\sin(\alpha_0 t))} e^{-kz\Im(\alpha_0 t)}
\]

(A.41)

\(\Re\) and \(\Im\) denote the real and imaginary parts respectively. Only the lowest-order terms in the coefficients of \(x\) and \(z\) were kept in the small-angle approximation.

This shows that at small incident angles, the transmitted field consists of a wave that travels approximately parallel to the interface (i.e. the transmitted wavevector \(\vec{k}_t\) makes angle \(\Re(\alpha_t)\) with the interface, which is small when the incident angle is small - see figure A.9c), and decays in amplitude and intensity with penetration depths \(1/k\Im(\alpha_t)\) and \(1/2k\Im(\alpha_t)\) respectively. This wave is known as the evanescent wave.

The critical angle is the incident angle at which, in the special case of no absorption \((\beta = 0)\), the resulting evanescent wave will travel parallel to the interface. Therefore the critical angle is determined by calculating the value of \(\alpha_i\) which will enforce \(\Re(\alpha_i) = 0\) in equation A.40. With \(\beta = 0\), the critical angle is easily calculated as:

\[
\alpha_c = \sqrt{2\delta}.
\]

(A.42)

From equation A.35, in the special case where there is no absorption \((\beta = 0)\), \(n\) is expressed as \(n = 1 - \delta\). \(\delta\) can be calculated using equation A.34, and for the experiments to be presented here, has a value of roughly \(3 \times 10^{-6}\) (based on a tetracene unit cell volume of \(573\text{\AA}^3\) [59], with 240 electrons per unit cell, and an X-ray
wavelength of 1.24˚A). The critical angle for the experiments to be presented here will therefore have a value of approximately 2.5mrad.

### A.2.4 Behaviour of the Evanescent Wave near the Critical Angle

We can now go about calculating the amplitude and penetration depth of the evanescent wave. By employing Maxwell’s equations, along with the boundary conditions for an electromagnetic field, we obtain the Fresnel Equations, which relate the amplitudes of the transmitted and reflected fields for a beam which is incident on the interface (see section 7.4 of reference [134] for a derivation):

\[
\begin{align*}
    t_\perp &= \frac{E_{t\perp}}{E_{0\perp}} = \frac{2n_1 \sin(\alpha_i)}{n_1 \sin(\alpha_i) + \frac{\mu_1}{\mu_2} \sqrt{n_2^2 - n_1^2 \cos^2 \alpha_i}} \\
    t_\parallel &= \frac{E_{t\parallel}}{E_{0\parallel}} = \frac{2n_1 \mu_2}{n_2 \sin(\alpha_i) + n_1 \sqrt{n_2^2 - n_1^2 \cos^2 \alpha_i}} \\
    r_\perp &= \frac{E_{r\perp}}{E_{0\perp}} = \frac{n_1 \sin(\alpha_i) - \frac{\mu_1}{\mu_2} \sqrt{n_2^2 - n_1^2 \cos^2 \alpha_i}}{n_1 \sin(\alpha_i) + \frac{\mu_1}{\mu_2} \sqrt{n_2^2 - n_1^2 \cos^2 \alpha_i}} \\
    r_\parallel &= \frac{E_{r\parallel}}{E_{0\parallel}} = \frac{\mu_2 n_2^2 \sin(\alpha_i) - n_1 \sqrt{n_2^2 - n_1^2 \cos^2 \alpha_i}}{\mu_2 n_2^2 \sin(\alpha_i) + n_1 \sqrt{n_2^2 - n_1^2 \cos^2 \alpha_i}}
\end{align*}
\]

(A.43)

The variables are defined in figure A.8. Notice that the components of the fields which are parallel (\(E_\parallel\)) and perpendicular (\(E_\perp\)) to the plane of incidence will have different transmission and reflection coefficients. However, for X-rays passing from air (\(n \approx 1\)) to a material with index \(n = 1 - \delta + i\beta\), assuming non-magnetic materials so that \(\mu_1 \approx \mu_2 \approx \mu_0\), the polarization of the beam becomes irrelevant, and the parallel and perpendicular components yield the same values.
We are interested in the behaviour near the critical angle, which is on the order of milliradians. Therefore, the small angle approximation can be applied. In these conditions, the Fresnel Equations reduce to the following:

\[
\begin{align*}
t &= \frac{E_t}{E_0} = \frac{2\alpha_i/\alpha_c}{\alpha_i/\alpha_c + \sqrt{(\alpha_i/\alpha_c)^2 - 1 + 2i\beta/\alpha_c^2}} \quad (A.44) \\
r &= \frac{E_r}{E_0} = \frac{\alpha_i/\alpha_c - \sqrt{(\alpha_i/\alpha_c)^2 - 1 + 2i\beta/\alpha_c^2}}{\alpha_i/\alpha_c + \sqrt{(\alpha_i/\alpha_c)^2 - 1 + 2i\beta/\alpha_c^2}} \quad (A.45)
\end{align*}
\]

Note that equation A.42 was substituted in order to express the equations in terms of the critical angle.

The intensity transmission coefficient, which is defined as the ratio of intensities between the transmitted and incident waves, is calculated as \( T = |t|^2 \), where \( t \) is given by equation A.44. \( T \) is plotted in figure A.9a for various values of the decay parameter \( \beta/\alpha_c^2 \). Notice that when the incident beam is at the critical angle, the evanescent wave is four times the intensity of the incident wave in the optimal case of no absorption. This shows that the critical angle optimizes the intensity of the evanescent wave, which is the source of the diffracted wave. Therefore the critical angle is a convenient target when attempting to optimize the diffracted intensity in a GIXD experiment.

The intensity penetration depth, as described above, may also be calculated, and is expressed as

\[
\Lambda = \frac{1}{2k3(\alpha_t)}. \quad (A.46)
\]

Here, the transmission angle \( \alpha_t \) can be calculated by applying the small-angle ap-
Figure A.9: a) Variation of the transmission coefficient with incident beam angle in the vicinity of the critical angle. b) Variation of the X-ray penetration depth with incident angle. c) The real part of the transmission angle $\alpha_t$, which in the small-angle approximation represents the angle that the evanescent wave makes with the interface. The plots are shown for several values of the absorption parameter $\beta/\alpha^2_c$. The legend applies to all plots.
proximation to Snells law, given in equation A.40. The imaginary part of equation A.40 is numerically calculated and used in equation A.46 to plot the dimensionless quantity \( \Lambda \cdot 2k\alpha_c = \frac{1}{3\sqrt{\left(\frac{\alpha_i}{\alpha_c}\right)^2 - 1 + 2i\frac{\beta}{\alpha_c}}} \) in figure A.9b for various values of the absorption term \( \beta/\alpha_c^2 \). The real part of \( \alpha_t \), which represents the actual angle that the evanescent wave makes with the interface (see equation A.41), is plotted in figure A.9c.

Clearly, the penetration depth is extremely sensitive to the incident angle when near the critical angle. This must be kept in mind if one wishes to enhance surface sensitivity in an experiment. The absorption term \( \beta/\alpha_c^2 \) can vary substantially, depending on the material. A table of these values can be found in table 3.1 of reference [97]. For example, for silicon at an X-ray wavelength of 1.54Å, the value for \( \beta/\alpha_c^2 \) is 0.0115. From figure A.9b, this results in a value of \( \Lambda \cdot 2k\alpha_c \sim 10 \), which translates to a penetration depth of a few hundred angstroms at the critical angle.
Appendix B

Mapping Diffractometer Angles to Reciprocal-Space Coordinates

In the GIXD experiments described in this thesis, a diffractometer is used to precisely control the orientation of a sample and detector with respect to an incident X-ray beam. This is accomplished by suitable specification of the positions of the diffractometer circles (expressed as angles) depicted in figure B.1. For particular orientations of the sample and detector, intensity measurements will correspond to a particular point in reciprocal-space. In this appendix, we derive the equations which are used to map diffractometer angles to reciprocal-space coordinates.
Figure B.1: Labelling convention for the diffractometer angles. The various circles are labelled with Greek letters (black letters indicate circles for detector positioning, and grey indicate those for sample positioning), and the directions of positive rotation are indicated by the red arrows. The blue axes indicate the definitions of the laboratory frame coordinates. The incident beam polarization vector $\vec{E}$, which is horizontal with respect to the lab frame, is also indicated.
B.1 Definitions of the Diffractometer Angles

Detector Angles

Figure B.1 shows, schematically, six of the eight possible angles that may be adjusted. Two of these are used to control the detector orientation, and the remainder are dedicated to sample positioning.

The functions of the detector angles are highlighted in figure B.2. The position of the detector arm with respect to the incident beam is entirely determined by the angles $\nu$ and $\delta$. $\nu$ determines the azimuthal angle (in the laboratory reference frame) that the detector arm makes with the incident beam (i.e. the angle between the incident beam, and the projection of the detector arm on the horizontal plane), and $\delta$ specifies the vertical angle that the detector arm makes with the horizontal plane. Note from the figure that the incident wavevector $\vec{k}$ corresponds to the $-\hat{x}_L$ direction, and the diffracted wavevector $\vec{k}'$ corresponds to the orientation of the detector arm. Therefore, using the subscript ‘$L$’ to denote specification of coordinates in the laboratory reference frame, we can express $\vec{k}$ and $\vec{k}'$ as follows:

$$\vec{k} = -k\hat{x}_L$$  \hspace{1cm} (B.1)

$$\vec{k}' = -k \cos(\delta) \cos(\nu) \hat{x}_L - k \cos(\delta) \sin(\nu) \hat{y}_L + k \sin(\delta) \hat{z}_L$$  \hspace{1cm} (B.2)

Therefore, the expression for the scattering vector $\vec{Q}$ in the lab frame is:

$$\vec{Q} = \vec{k}' - \vec{k} = k(1 - \cos(\delta) \cos(\nu)) \hat{x}_L - k \cos(\delta) \sin(\nu) \hat{y}_L + k \sin(\delta) \hat{z}_L$$  \hspace{1cm} (B.3)
Figure B.2: Definitions of the angles used to position the X-ray detector with respect to the incident beam.
Sample Angles

The other four circles shown in figure B.1 determine the sample orientation with respect to the incident beam. As can be seen in the figure, there is a hierarchy of dependencies for these circles, meaning that the orientation of any circle depends on the circles which precede it in the hierarchy. Conversely, a rotation of any circle changes the orientations of the circles below it in the hierarchy. The order of this hierarchy is: $\mu$, $\eta$, $\chi$, and $\phi$.

The order of the hierarchy, and the actions of each circle must be accounted for in our derivation. The first circle in the hierarchy is $\mu$. This circle rotates the entire sample positioning assembly about the $\hat{z}$ axis in the lab frame. The next circle is $\eta$, which rotates the sample assembly about a horizontal axis in the lab frame, the position of which depends on $\mu$. The next circle is $\chi$, which rotates the sample about an axis which is parallel to the plane of the $\eta$ circle. The final circle is $\phi$, which rotates the sample about an axis which is parallel to the plane of the $\chi$ circle.

So far, six of the eight circles have been mentioned. The remaining two are fixed on the $\phi$ circle, and are usually used to remove sample ”wedges” (i.e. to ensure that the sample surface is always parallel to the $\phi$ axis). For the rest of this discussion, it will be assumed that these circles are appropriately set so that this is the case, and we will therefore neglect them in the calculation.

B.2 Derivation of the General Equations

For the purposes of the calculations presented in this section, the definitions of the zero-positions of the sample positioning circles are shown in figure B.3, along with
their directions of positive rotation.

Our objective is to derive an expression for the reciprocal-space coordinates of $\vec{Q}$ in terms of all of the diffractometer angles. That is, we want to know what point in reciprocal-space is being measured for a particular set of diffractometer circle positions. Since reciprocal-space is fixed with respect to the sample, our goal is to find the coordinates of $\vec{Q}$ in a reference frame which is stationary with respect to the sample. We therefore approach the problem by carrying out the following steps:

1. Define a sample reference frame which will remain fixed with respect to the sample. The basis vectors in this frame will be denoted by $\hat{x}_S$, $\hat{y}_S$ and $\hat{z}_S$.

2. Calculate the orientations of these sample basis vectors in the lab frame after rotation of the diffractometer circles.

3. Determine the components of $\vec{Q}$ in the sample frame by calculating its components along each of the sample basis vectors.

**Definition of the Sample Reference Frame**

The sample coordinates will be defined such that, when all sample-positioning diffractometer angles are set to zero, the sample coordinates will be coincident with the lab coordinates shown in figures B.2 and B.3. Thus, at $\mu = \eta = \chi = \phi = 0^\circ$, the sample coordinates can be expressed as

$$
\hat{x}_s(\mu = \eta = \chi = \phi = 0) = \hat{x}_L
$$

$$
\hat{y}_s(\mu = \eta = \chi = \phi = 0) = \hat{y}_L
$$

$$
\hat{z}_s(\mu = \eta = \chi = \phi = 0) = \hat{z}_L
$$

(B.4)
Figure B.3: Definition of the zero-positions for the sample-manipulating diffractometer circles. The configuration shown is valid when all four sample-manipulating angles ($\mu$, $\eta$, $\chi$, and $\phi$) are set to their zero positions. The circling arrows indicate the directions of positive rotation for each circle.
Calculation of the Sample Basis-Vectors after Rotation

In order to determine the positions of the sample axes in the lab frame, we will need to make use of rotation matrices. The following matrices, when applied to an arbitrary vector, have the effect of rotating the vector by a positive (as defined by the right hand rule) angle $\theta$ about the $x$, $y$, or $z$ axis, respectively:

$$R_x(\theta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta) & -\sin(\theta) \\ 0 & \sin(\theta) & \cos(\theta) \end{bmatrix} \tag{B.5}$$

$$R_y(\theta) = \begin{bmatrix} \cos(\theta) & 0 & \sin(\theta) \\ 0 & 1 & 0 \\ -\sin(\theta) & 0 & \cos(\theta) \end{bmatrix} \tag{B.6}$$

$$R_z(\theta) = \begin{bmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{B.7}$$

Hereafter, we will take these matrices to be defined on the basis of the lab frame.

We start with a rotation of the $\phi$ circle, since this circle is the lowest in the hierarchy, and can only operate independently of the other circles if they are in their zero-positions. From the zero position in figure B.3, a rotation of $\phi$ will have the effect of rotating each of the sample axes in a negative direction about the $\hat{z}_L$ axis. Therefore, using equation B.7, we apply a rotation matrix which represents $R_z(-\phi)$
We now repeat this step using the $\chi$ circle. Again referring to figure B.3, with $\mu = \eta = 0$, a rotation in $\chi$ is a negative rotation about the $\hat{x}_L$ axis. Therefore we can simply apply $R_x(-\chi)$ (equation B.5) to get;

\[
\hat{x}_s(\mu = \eta = 0, \chi, \phi) = R_x(-\chi) \cdot \hat{x}_s(\mu = \eta = 0, \phi) \\
= R_x(-\chi) \cdot R_z(-\phi) \cdot \hat{x}_L 
\]

(B.11)

\[
\hat{y}_s(\mu = \eta = 0, \chi, \phi) = R_x(-\chi) \cdot \hat{y}_s(\mu = \eta = 0, \phi) \\
= R_x(-\chi) \cdot R_z(-\phi) \cdot \hat{y}_L 
\]

(B.12)

\[
\hat{z}_s(\mu = \eta = 0, \chi, \phi) = R_x(-\chi) \cdot \hat{z}_s(\mu = \eta = 0, \phi) \\
= R_x(-\chi) \cdot R_z(-\phi) \cdot \hat{z}_L 
\]

(B.13)

Proceeding in the same manner for the circle $\eta$ which, with $\mu = 0$, results in a
positive rotation about the lab $\hat{y}_L$ axis, we get

\[
\hat{x}_s(\mu = 0, \eta, \chi, \phi) = R_y(\eta) \cdot \hat{x}_s(\mu = \eta = 0, \chi, \phi) \\
= R_y(\eta) \cdot R_x(-\chi) \cdot R_z(-\phi) \cdot \hat{x}_L \\
(\text{B.14})
\]

\[
\hat{y}_s(\mu = 0, \eta, \chi, \phi) = R_y(\eta) \cdot \hat{y}_s(\mu = \eta = 0, \chi, \phi) \\
= R_y(\eta) \cdot R_x(-\chi) \cdot R_z(-\phi) \cdot \hat{y}_L \\
(\text{B.15})
\]

\[
\hat{z}_s(\mu = 0, \eta, \chi, \phi) = R_y(\eta) \cdot \hat{z}_s(\mu = \eta = 0, \chi, \phi) \\
= R_y(\eta) \cdot R_x(-\chi) \cdot R_z(-\phi) \cdot \hat{z}_L \\
(\text{B.16})
\]

Finally, we rotate the sample using $\mu$, which results in a positive rotation about the lab $\hat{z}_L$ axis. Therefore, the final expressions for the sample coordinate axes in the laboratory frame are

\[
\begin{aligned}
\hat{x}_s(\mu, \eta, \chi, \phi) &= R_z(\mu) \cdot R_y(\eta) \cdot R_x(-\chi) \cdot R_z(-\phi) \cdot \hat{x}_L \\
\hat{y}_s(\mu, \eta, \chi, \phi) &= R_z(\mu) \cdot R_y(\eta) \cdot R_x(-\chi) \cdot R_z(-\phi) \cdot \hat{y}_L \\
\hat{z}_s(\mu, \eta, \chi, \phi) &= R_z(\mu) \cdot R_y(\eta) \cdot R_x(-\chi) \cdot R_z(-\phi) \cdot \hat{z}_L \\
(\text{B.17})
\end{aligned}
\]

Determining $\vec{Q}$ in the Sample Frame

We may now determine the components of $\vec{Q}$ in the sample frame by projecting it onto the sample coordinate axes:

\[
\vec{Q} = (\vec{Q} \cdot \hat{x}_s)\hat{x}_s + (\vec{Q} \cdot \hat{y}_s)\hat{y}_s + (\vec{Q} \cdot \hat{z}_s)\hat{z}_s \\
(\text{B.18})
\]

We therefore obtain the following matrix expressions for the components of $\vec{Q}$ in
Here, $\vec{Q}^T$ is the scattering vector $\vec{Q}$ from equation B.3 expressed as a row-vector:

$$\vec{Q}^T = \begin{bmatrix} k(1 - \cos(\delta) \cos(\nu)) & -k \cos(\delta) \sin(\nu) & k \sin(\delta) \end{bmatrix}, \quad (B.20)$$

and the matrix $R_{tot}(\mu, \eta, \chi, \phi)$ is the product of the four rotation matrices in equations B.17, as follows:

$$R_{tot}(\mu, \eta, \chi, \phi) = R_z(\mu) \cdot R_y(\eta) \cdot R_x(-\chi) \cdot R_z(-\phi)$$

Lastly, the three lab-frame basis vectors, for the purposes of equation B.19, are respectively expressed as

$$\hat{x}_L = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad \hat{y}_L = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \hat{z}_L = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \quad (B.22)$$
After substitution of B.22 into B.19, we obtain the following final expression for \( \mathbf{\tilde{Q}} \) expressed on the basis of the sample coordinate frame.

\[
\mathbf{\tilde{Q}}_s^T = \mathbf{\tilde{Q}}_L^T \cdot \mathbf{R}_{tot}
\]  

(B.23)

Here, the subscripts \( S \) and \( L \) denote representation on the basis of, respectively, sample frame and lab frame coordinates.

Clearly, equation B.23 can become very complicated when expanded. In the next section, we simplify this equation for the special case of the vertical scattering geometry used in the experiments presented in this thesis.

### B.3 Reciprocal-Space Mapping under Vertical Scattering Geometry

As discussed in section 3.2.2, for the GIXD experiments presented in this thesis, the sample was held vertically while measurements were conducted. This geometry is as illustrated in figure B.1. In this vertical configuration, \( \chi \) has a value of \(-\pi/2\), and \( \mathbf{\tilde{R}}_{tot} \) takes on the following simplified form:

\[
\mathbf{\tilde{R}}_{tot}(\mu, \eta, \chi = -\pi/2, \phi) = \begin{bmatrix}
\cos(\mu) \cos(\eta + \phi) & \cos(\mu) \sin(\eta + \phi) & \sin(\mu) \\
\sin(\mu) \cos(\eta + \phi) & \sin(\mu) \sin(\eta + \phi) & -\cos(\mu) \\
-\sin(\eta + \phi) & \cos(\eta + \phi) & 0
\end{bmatrix}
\]  

(B.24)

Using equation B.23, the components of \( \mathbf{\tilde{Q}}_s \) for this geometry can be expressed as
follows:

\[
\begin{bmatrix}
Q_{xs} \\
Q_{ys} \\
Q_{zs}
\end{bmatrix} =
\begin{bmatrix}
-k \cos(\nu - \mu) \cos(\eta + \phi) \cos(\delta) + k \cos(\mu) \cos(\eta + \phi) - k \sin(\delta) \sin(\eta + \phi) \\
-k \cos(\nu - \mu) \sin(\eta + \phi) \cos(\delta) + k \cos(\mu) \sin(\eta + \phi) + k \sin(\delta) \cos(\eta + \phi) \\
-k \sin(\nu - \mu) \cos(\delta) + k \sin(\mu)
\end{bmatrix}
\]

(B.25)

In this geometry, the angle \( \mu \) may be used to control the incident angle of the X-ray beam. For grazing incidence, \( \mu \) will be small in order to maximize surface sensitivity. It is also practical to set \( \nu = \mu \) so that the detector arm will be parallel to the sample surface, and only in-plane diffraction peaks will be detected. Under this condition, we can expand to first-order in \( \mu \), and B.25 can be simplified to

\[
\begin{bmatrix}
Q_{xs} \\
Q_{ys} \\
Q_{zs}
\end{bmatrix} =
\begin{bmatrix}
-k \cos(\eta + \phi) \cos(\delta) + k \cos(\eta + \phi) - k \sin(\delta) \sin(\eta + \phi) \\
-k \sin(\eta + \phi) \cos(\delta) + k \sin(\eta + \phi) + k \sin(\delta) \cos(\eta + \phi) \\
k \sin(\nu - \mu) \cos(\delta) + k \sin(\mu)
\end{bmatrix}
\]

(B.26)

Notice that, to first-order, the in-plane components of \( \vec{Q}_s \) do not depend on the incident angle \( \mu \). Also notice, as might have been inferred from the figures, that \( \eta \) and \( \phi \) have equivalent roles in this geometry, and we therefore set \( \phi = 0^\circ \) and
manipulate the $\eta$ circle only. This leaves the following simplified expression for $\mathbf{Q}_S$:

$$
\begin{bmatrix}
Q_{x_S} \\
Q_{y_S} \\
Q_{z_S}
\end{bmatrix} =
\begin{bmatrix}
-k \cos(\eta) \cos(\delta) + k \cos(\eta) - k \sin(\delta) \sin(\eta) \\
-k \sin(\eta) \cos(\delta) + k \sin(\eta) + k \sin(\delta) \cos(\eta) \\
2k \sin(\frac{\delta}{2}) \sin(\frac{\delta}{2} - \eta) \\
2k \sin(\frac{\delta}{2}) \cos(\frac{\delta}{2} - \eta) \\
k\mu
\end{bmatrix}
$$

(B.27)
Appendix C

Determination of the Reciprocal Lattice Vectors from the Standard Lattice Parameters

Here it is shown how the conventional lattice parameters, as defined in figure 1.3, can be used to calculate the components and in-plane magnitudes of the reciprocal lattice vectors.

To begin, we define the components of the direct lattice vectors within an arbitrary coordinate frame. The coordinate frame is selected such that \( \vec{a} \) is coincident with the \( x \) axis, and \( \vec{b} \) lies within the \( x-y \) plane. Under this coordinate frame, the lattice vectors
are as follows:

\[
\vec{a} = a \cdot (1, 0, 0) \\
\vec{b} = b \cdot (\cos(\gamma), \sin(\gamma), 0) \\
\vec{c} = c \cdot \left( \frac{c_x}{c}, \frac{c_y}{c}, \frac{c_z}{c} \right)
\] (C.1)

The components of the vector \(\vec{c}\) are chosen such that \(\vec{c}\) makes angles of \(\alpha\) and \(\beta\) with \(\vec{b}\) and \(\vec{a}\) respectively (to match the definitions of these lattice parameters), and such that the magnitude of \(\vec{c}\) is just \(c\). This results in the following expressions for the components of \(\vec{c}\):

\[
\frac{c_x}{c} = \cos(\beta) \\
\frac{c_y}{c} = \frac{1}{\sin(\gamma)} \left( \cos(\alpha) - \cos(\beta) \cos(\gamma) \right) \\
\frac{c_z}{c} = \sqrt{1 - \cos^2(\beta) - \frac{1}{\sin^2(\gamma)} \left( \cos(\alpha) - \cos(\beta) \cos(\gamma) \right)^2}
\] (C.2)

The reciprocal lattice vectors are fairly straightforward to calculate using equation A.8. The following expressions are obtained:

\[
\vec{a}^* = \frac{2\pi}{a \sin(\gamma)} \cdot \left( \sin(\gamma), -\cos(\gamma), \frac{c_y}{c_z} \cos(\gamma) - \frac{c_x}{c_z} \sin(\gamma) \right) \\
\vec{b}^* = \frac{2\pi}{b \sin(\gamma)} \cdot \left( 0, 1, -\frac{c_y}{c_z} \right) \\
\vec{c}^* = \frac{2\pi}{c_z} \cdot (0, 0, 1)
\] (C.3)

For the analysis described in this thesis, it is of interest to consider only the in-plane components of a reciprocal lattice vector of the form \(\vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*\).
We denote this component by $\vec{G}_{hk,\parallel}$ in recognition of the fact that it is parallel to the a-b plane, and the fact that this component has no dependence on $l$. By taking only the in-plane components of $\vec{G}_{hkl}$, it is expressed as follows:

$$\vec{G}_{hk,\parallel} = \frac{2\pi}{\sin(\gamma)} \cdot \left( h \frac{\sin(\gamma)}{a}, -h \frac{\cos(\gamma)}{a} + k \frac{1}{b} \right) \quad (C.4)$$

Finally, we can write the magnitude of the in-plane component of $\vec{G}_{hkl}$ as follows:

$$|\vec{G}_{hk,\parallel}| = \frac{2\pi}{ab \sin(\gamma)} \sqrt{h^2 b^2 + k^2 a^2 - 2hkab \cos(\gamma)} \quad (C.5)$$
Appendix D

Diffractometer and Sample Alignment

As discussed in chapters A and 3, the GIXD experiments require the measurement of diffracted intensity at very precise values of the scattering vector $\vec{Q} = \vec{k}' - \vec{k}$, which is related to the sample and detector orientation through the incident and scattered wavevectors $\vec{k}$ and $\vec{k}'$. Therefore, we require the ability to accurately control the orientation of the sample and detector with respect to the incident beam. This requires ensuring that the incident beam is properly centered on the sample, with the incident angle precisely known, and ensuring that the center of rotation of the detector matches the point at which the beam strikes the sample. The procedures for aligning the sample and diffractometer to achieve these goals depend on the details of the experimental apparatus being used. Here, we describe the procedure used for the apparatus at the APS facility.

A schematic diagram of the diffractometer, indicating the circles of rotation and their assigned symbols, is shown in figure 3.4 on page 37. Two circles, $\nu$ and $\delta$
are responsible for controlling the detector orientation, while the rest determine the sample orientation. The rotation axes for all circles intersect at a common point, that is, at the rotation center of the diffractometer. In the alignment procedure, we first ensure that the incident beam passes through the rotation center. We then carefully align the sample surface to be parallel to the plane of rotation of the $\eta$ circle (see figure 3.4). Finally, we ensure that the sample surface is centered in the incident beam, and hence at the position of the diffractometer rotation center.

**Aligning the Diffractometer Rotation Center with the Incident Beam**

In order to align the diffractometer rotation center with the incident beam, the position of the incident beam must be determined. This is accomplished using Kodak Linagraph paper (or “burn paper”) which will darken when exposed to the X-ray beam. The paper is placed on the detector arm, with the arm in the downstream position ($\delta = 0^\circ$) with respect to the incident beam (see figure D.1). By suitable adjustment of the slits, the beam is allowed to make a cross-shape on the linagraph paper (i.e. a “burn mark”) in order to indicate the position of the beam. Then the detector arm is rotated to the upstream position ($\delta = 180^\circ$) where a second cross is burned. As shown in figure D.1, the height difference between the crosses will be twice the distance between the diffractometer center and the beam height, and so the diffractometer height can be raised or lowered accordingly.

The diffractometer rotation center will now be vertically aligned with the beam. In order to perform the horizontal alignment, a similar process may be carried out using the $\nu$ circle in place of the $\delta$ circle.
Figure D.1: Illustration of the procedure for vertically aligning the diffractometer with the X-ray beam. “Burn marks” are made on Kodak Linagraph paper with the detector in two opposite positions on the $\delta$ circle. The resulting vertical separation of the marks on the burn paper will be twice the distance that the diffractometer must be raised or lowered in order to be centered with the beam. Note that although the detector arm is shown here as being parallel to the beam, the procedure will also work if the arm is slightly tilted with respect to the beam (The distance between burn marks can be shown to be $2\Delta y/\cos(\alpha)$, where $\alpha$ is the tilt angle of the detector arm. Therefore this approximation is correct if terms of second-order in $\alpha$ can be neglected.).
Aligning the Sample Surface with the Diffractometer Circles

The next step is to align the sample surface with the diffractometer circles, such that a rotation in \( \eta \) (see figure 3.4) maintains the orientation of the sample surface normal. The sample is mounted to the sample holder (which can be seen in figure 3.6b) by two-sided tape, which can introduce some variability in the precise orientation of the surface. Due to this variability, the sample alignment procedure must be repeated each time a new sample is mounted.

The sample surface alignment is performed with the aid of a visible laser beam. The laser is allowed to reflect from the sample surface, and onto a nearby wall. The \( \eta \) circle is then manually rotated in order to observe the resulting change in position of the reflected laser spot. If the sample is properly aligned, the spot will not move as \( \eta \) is rotated. If there is a “wedge” angle (i.e. if the sample and \( \eta \) circle are not aligned), then the laser spot will trace out an ellipse as \( \eta \) rotates.

After the path of the ellipse is observed, the orientation of the sample holder is adjusted so that the laser spot falls at the center of the ellipse. The sample holder in figure 3.6b is equipped with two motors to control its pitch and rotation, which can be adjusted to move the laser spot as desired. The \( \eta \) circle is then rotated again to check the new alignment, and the process is repeated iteratively until the alignment is acceptable.

Centering the Sample in the Diffractometer

The last step before measurements can be taken is to center the sample surface within the X-ray beam. Since at this point the beam is already aligned with the diffractometer center, the sample simply needs to be moved, along the \( \eta \) circle rotation-axis, into
the beam to center it within the diffractometer. At the same time, any offset in the circle $\mu$ can be eliminated. As depicted in figure 3.4, the sample surface is held vertically throughout the experiment (this orientation will help to enhance the diffracted intensity, as discussed below). Therefore, $\mu$ controls the X-ray beam incident angle.

The process of sample positioning is illustrated in figure D.2. The sample is translated along its normal until it begins to eclipse the beam, as can be determined by measuring the beam intensity in the detector positioned behind the sample. When the intensity is reduced by half, a rotation of $\mu$ can increase the detected intensity if the sample surface is not parallel to the incident beam. Therefore, $\mu$ is adjusted until the detected intensity is maximized. The process then repeats iteratively until, simultaneously, the sample is eclipsing the beam by one half, and a rotation of $\mu$ in any direction decreases the detected intensity. This indicates that the sample surface is properly positioned in the incident beam. The resulting position for the $\mu$ circle is calibrated to be the $\mu = 0^\circ$ position so that $\mu$ can then be used to specify the incident beam angle.
Figure D.2: An iterative process for positioning the sample in the middle of the X-ray beam with its surface parallel to the beam. 

a) The sample is translated until it eclipses the beam by one half, as determined by the intensity measurement.

b) The sample is rotated by adjusting the $\mu$ circle until the beam is minimally eclipsed, yielding a maximum intensity measurement.

c) The first two steps are iteratively repeated until no further improvement can be made. The sample is now aligned and centered in the beam.
Appendix E

Numerical Calculations of the Peak Intensities for Bulk Tetracene

In the GIXD experiments presented in chapter 4, in-plane diffraction peaks were sought out for a crystalline tetracene film. These experiments required predictions for the locations of the most intense diffraction peaks in order to provide a starting point for the searching procedure, which required knowledge of which peaks would be most intense, and thus easiest to detect. In order to make these predictions, the diffracted intensities for the lowest-order, in-plane diffraction peaks were calculated. In this chapter, this calculation is described.

E.1 Method of Calculation

In appendix A, it was shown that the diffracted intensity from a crystal is proportional to the squared magnitude of the unit-cell structure-factor (see equation A.9). Therefore, in order to calculate the relative intensity of a particular diffraction peak
at position $\mathbf{G}_{hkl}$, we only need to calculate the structure factor $F(\mathbf{G}_{hkl})$.

The structure factor can be calculated through equation A.18, and depends on the coordinates and form factors of all the atoms in the unit cell. For these intensity calculations, the atomic coordinates reported by Holmes and co-workers [59] were used. For simplicity, the $\mathbf{Q}$-dependence of the atomic form factor was ignored, and the value at $\mathbf{Q} = 0$ was used (this is numerically equal to the atomic number $Z$ of the atom - see equation A.15). The code used to perform the calculation is given in section E.3.

### E.2 Calculated Intensities

The results of the calculation are presented in table E.1. The peaks are listed in order of increasing $|\mathbf{G}_{hk\parallel}|^2$ (and hence increasing diffraction angle $\delta$). The quoted values of $\delta$ indicate the expected value of the diffractometer angle at which the peak is expected to be located.

As can be seen from the table, the highest intensity peaks have indices (11), (20) and (21) (highlighted rows in the table). These peaks are much stronger in intensity than the other peaks, and are therefore the most easily detectable. For this reason, all of the GIXD data presented in chapter 4 are based on these peaks.

### E.3 Maple Code

The code below was written in Maple 12 [135], and was used to calculate the diffracted intensities listed in table E.1 (note that commented lines begin with a ‘#’). The atomic coordinates in the program were taken from those reported by Holmes and co-
Table E.1: Table of calculated intensities for the lowest-order in-plane diffraction peaks of bulk tetracene. The highlighted rows indicate the three most intense peaks, which were used for the experiments in this thesis. The peak indices follow the axis labelling convention defined in this thesis (see section 1.2).

| Peak Index (hk) | $|G_{hk,\parallel}|^2$ (Å$^{-1}$) | $\delta$ (degrees) | Intensity (arbitrary units) |
|----------------|-------------------------------|--------------------|----------------------------|
| (10)           | 0.823                         | 9.313              | 7.64                       |
| (01)           | 1.090                         | 12.350             | 12.2                       |
| (11)           | 1.362                         | 15.450             | 507                        |
| (11)           | 1.369                         | 15.529             | 8148                       |
| (20)           | 1.645                         | 18.688             | 1735                       |
| (21)           | 1.969                         | 22.406             | 70.1                       |
| (21)           | 1.979                         | 22.517             | 11859                      |
| (02)           | 2.180                         | 24.847             | 266                        |
| (12)           | 2.326                         | 26.540             | 50.5                       |
| (12)           | 2.334                         | 26.635             | 148                        |
| (30)           | 2.468                         | 28.191             | 0.531                      |
| (31)           | 2.693                         | 30.819             | 114                        |
| (31)           | 2.703                         | 30.943             | 40.5                       |
| (22)           | 2.724                         | 31.190             | 176                        |
| (22)           | 2.738                         | 31.354             | 393                        |
workers [59], and published in the Cambridge Structural Database (CCDC deposition number 114446). As verification that the coordinates were entered correctly, Maple was used to plot atoms at the coordinates, as shown in figure E.1.

It is important to note that the coordinates used in this program correspond to the axis labelling convention used by Holmes and co-workers, and not that used in this thesis. The main difference between the two conventions is that the lattice vectors \( \vec{a} \) and \( \vec{b} \) are interchanged.

```plaintext
#Here, the internal memory is cleared, and the required packages are loaded.
restart;
with(plottools):
with(CurveFitting):
with(LinearAlgebra):

#Definition of the lattice parameters.
ap := 6.0565; bp := 7.8376; cp := 13.0104;
alpha := 77.127*Pi*(1/180);
beta := 72.118*Pi*(1/180);
gam := 85.792*Pi*(1/180);

#Definition of the lattice vectors.
a := array(1..3, [ap, 0, 0]);
b := array(1..3, [bp*cos(gam), bp*sin(gam), 0]);
c := array(1..3, [cp*cos(beta), cp*(cos(alpha)-cos(beta)*cos(gam))/sin(gam), cp*sqrt(1-cos(beta)^2-(cos(alpha)-cos(beta)*cos(gam))^2)/sin(gam)^2)];

#Here an array is defined which contains the coordinates of all 36 carbon atoms in the unit cell.
carbon := array(1..36, 1..3, [[-5.65, 3.768, -1.652],
[.363, 4.349, -2.511], [.134, 4.47, -3.912], [1.07, 5.027, -4.741], [2.296, 5.52, -4.197], [2.55, 5.441, -2.877],
[1.617, 4.852, -1.97], [1.837, 4.738, -0.605], [.337, 3.661, -.281], [.912, 4.156, .281], [1.14, 4.048, 1.652],
[.212, 3.467, 2.511], [.441, 3.346, 3.912], [-.495, 2.79, 1.652],
[.418, 2.79, 1.652], [-.495, 2.79, 1.652],
```
4.741], [-1.721, 2.297, 4.197], [-1.975, 2.376, 2.877], [-1.041, 2.965, 1.97], [-1.262, 3.078, .605], [-3.953, 1.007, -1.272], [-2.482, 1.655, -4.606], [-1.229, .971, -4.473], [-.909, .344, -3.33], [-1.797, .332, -2.211], [-1.498, -.346, -1.025], [-3.667, .343, -0.65e-1], [-2.104, -1.007, 1.272], [-2.988, -1.02, 2.34], [-2.695, -1.673, 3.578], [-3.575, -1.655, 4.606], [-4.827, -.971, 4.473], [-2.366, 1.908, 4.775], [-3.33, 2.732, 5.675], [1.26, 3.659, 4.278], [1.962, 4.379, 1.995], [-4.788, 1.454, -1.342], [-4.19, 2.127, -3.681], [-2.695, 2.097, -5.42], [-.619, .961, -5.202], [-0.72e-1, -1.101, -3.262], [-.661, -.758, -.943], [-5.396, .758, .943], [-5.985, .101, 3.2625], [-5.437, -.961, 5.202], [-3.361, -2.097, 5.42], [-1.867, -2.127, 3.681], [-1.268, -1.454, 1.342]]):

#This array contains the coordinates of all 24 hydrogen atoms in the unit cell.
hydrogen := array(1 .. 24, 1 .. 3, [[-1.387, 3.437, -1.995], [-.685, 4.157, -4.278], [.905, 5.084, -5.675], [2.942, 5.909, -4.775], [3.369, 5.785, -2.542], [2.654, 5.07, -2.52], [-2.794, 2.031, 2.542], [-2.078, 2.746, .252], [-2.366, 1.908, 4.775], [-3.33, 2.732, 5.675], [1.26, 3.659, 4.278], [1.962, 4.379, 1.995], [-4.788, 1.454, -1.342], [-4.19, 2.127, -3.681], [-2.695, 2.097, -5.42], [-.619, .961, -5.202], [-0.72e-1, -1.101, -3.262], [-.661, -.758, -.943], [-5.396, .758, .943], [-5.985, .101, 3.2625], [-5.437, -.961, 5.202], [-3.361, -2.097, 5.42], [-1.867, -2.127, 3.681], [-1.268, -1.454, 1.342]]):

#The following procedure performs the intensity calculation.
For a particular set of hkl indices, the procedure returns the squared magnitude of the structure factor:

#Declaration of the procedure
sfactor := proc(h,k,l)
    #Definition of all the reciprocal lattice vectors
    local as, bs, cs, F, n;
    as := <1.0374, -0.07638, -0.3260>:
    bs := <0, 0.8041, -0.1738>:
    cs := <0, 0, 0.5193>:
    F := 0: #Initializes the structure factor to zero
    #The following 'for' loop adds the contribution to the structure factor from each carbon atom. The factor of '6' represents the atomic form-factor for carbon.

231
for n from 1 to 36 do
    F := F + 6 * \exp(-I * \text{DotProduct}(h*as+k*bs+l*cs, <carbon[n,1], carbon[n,2], carbon[n,3]>));
end do:

# Now add the contribution from all the hydrogen atoms are added.
for n from 1 to 24 do
    F := F + \exp(-I * \text{DotProduct}(h*as+k*bs+l*cs, <hydrogen[n,1], hydrogen[n,2], hydrogen[n,3]>));
end do:

# Here the final result is returned.
return (abs(F)^2);
end proc:

When the "sfactor" procedure is called, the squared magnitude of the structure factor is returned. For example, the intensity of the (1\bar{1}) peak is calculated by calling the command "sfactor(1,-1,0);", which returns the number "8148.229281".
Figure E.1: Maple-generated plot of the atoms in the tetracene unit cell. The program placed spheres representing atoms at the coordinates that were entered for use in the intensity calculations. Atomic bonds were drawn in manually after the plot was generated. This plot was used to verify that the correct atomic coordinates had been entered.
Appendix F

The Deconvolution Algorithm

Included below is the code used to carry out the deconvolution procedure described in section 3.3.2. The code was run using Maple 12 [135]. Commented lines are initiated with a ‘#’ character. Only the portion of the program which computes the deconvolved data is shown here (code that is used for data formatting before processing is omitted).

#This procedure applies a Wiener filter to the raw data. The parameters are: i – an integer identifier for the data set to be processed; widthparameter – a parameter that is related to the inverse width of the point–spread–function (PSF); noise – an estimate for the RMS noise in the data .
#Declaration of the procedure.
wiener:=proc(i, widthparameter, noise)
    #declaration of some global and local variables that are used by the procedure
    global alldatadeconvolved, data, plotlist; local psf, N, psfseries, n, psfFourier, m, row, datafourier, filtered, minx, maxx, miny, maxy, minz, maxz, j, maxheightx, maxheighty, plotwidth;

# Definition of the PSF. It is expressed as a Gaussian curve, and is a function of ‘n’ (an index referring to the measurement number of a particular row of data). The multidimensional arrays ‘alldata’ contain the raw data, and the indexes are defined as follows: alldata[data set number][row number][column number][value index]. The ‘value index’ refers to one of three numbers that are contained in each measurement; the delta value, the eta value, and the normalized intensity.

\[
\text{psf} := n \rightarrow \exp(-\text{width parameter} \times (n \times (\text{alldata}[i][1][2][1] - \text{alldata}[i][1][1][1])^2))
\]

# Determine the number of measurements in the rows of data to be processed (will be needed for the loops).
N := nops(alldata[i][1]) :

# Here we convert the continuous PSF defined above into a discrete series to be applied to the data.
psfseries := [seq(0, k = 1..N)] ; # the psf begins as an empty array of zeros
for n from 1 to N do
    for m from 1 to N do
        psfFourier[n] := evalf(psffourier[n] +
            \[
            \exp(-(2 \times \text{Pi} \times I \times (n-1) \times (m-1)) / (N))
            \]
    end do :
end do :

# Calculate the discrete Fourier transform of the PSF
psffourier := [seq(0, k = 1..N)] ; # initialize the array to zero
for n from 1 to N do
    for m from 1 to N do
        psffourier[n] := evalf(psffourier[n] +
            \[
            \exp(-(2 \times \text{Pi} \times I \times (n-1) \times (m-1)) / (N))
            \]
    end do :
end do :

235
Here is where the deconvolution takes place. This code will deconvolve the data row-by-row. For each row, the discrete Fourier transform is calculated, then multiplied by the Wiener filter in Fourier space, and the product is inverse transformed to produce the deconvolved data row.

```plaintext
for row from 1 to nops(alldata[i]) do
    #Calculate the Fourier transform of the current row of data
datafourier:=[seq(0,k=1..N)]; #initialize the data row to zero
    for n from 1 to N do
        for m from 1 to N do
            datafourier[n]:= datafourier[n]+exp(-2*Pi*I*(n-1)*(m-1))/N)*alldata[i][row][m][3];
        end do:
    end do:
    #Now the filtered spectrum is calculated in Fourier space.
filtered:=[seq(0,k=1..N)]; #Initialize the filtered data array to zero.
    for n from 1 to N do
        #This line multiples the current value in the data array by the corresponding value in the Wiener filter array.
        filtered[n]:=(datafourier[n]*conjugate(psfFourier[n])*abs(datafourier[n])^2)/(abs(psfFourier[n])^2*abs(datafourier[n])^2+noise^2);
    end do:
    #Now we prepare for Inverse Fourier Transforming.
    #Initialize the deconvolved data row to zero.
    for n from 1 to N do
        alldatadeconvolved[i][row][n][3]:=0;
    end do:
```

236
# Now inverse transform the filtered row and copy it to the matrix of deconvolved data.

for n from 1 to N do
    for m from 1 to N do
        alldatadeconvolved[i][row][n][3] := alldatadeconvolved[i][row][n][3] + evalf(exp((2*Pi*I*(n-1)*(m-1))/(N))*filtered[m]):
    end do:
end do:

# Now eliminate any residual imaginary parts of the filtered image (which occur due to machine precision error).

for n from 1 to N do
    alldatadeconvolved[i][row][n][3] := Re(alldatadeconvolved[i][row][n][3]):
end do:

# When this loop terminates, the data has been filtered and stored in the array 'alldatadeconvolved[i]'.

end proc: