Direct determination of adsorbate positions with energy-dependent and angle-resolved photoelectron diffraction
by Huasheng Wu

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University
© Copyright by Huasheng Wu (1994)

Abstract:
The atomic structure of an interface governs most properties of the interface. For the first time, we successfully implemented a method to directly determine the adsorbate positions using energy-dependent and angle-resolved photoelectron diffraction. This method inverts the energy-dependent diffraction curves to 3-D real space, and then sums the results over all the emission directions to obtain the atomic image. The result for Si(111)\(\sqrt{3}\times\sqrt{3}\)-Al clearly shows the Si atoms around the emitter Al and identifies the Al as occupying the T4 site. This is the best atomic image ever published, with no twin image and with good atomic position values.

To further reduce the artifacts associated with this method, the angle dependence of the effective scattering factor was examined. The result suggests that the artifacts are from the large phase variation of this factor when the emission directions are far away from the emitter-scatterer direction. As a consequence, we introduced a new transform scheme - the small-cone method. To calculate the image function intensity at a given position vector in real space, we now use only those diffraction curves with their emission directions within a small cone, the axis of which is opposite to the given position vector. The width of the small cone can be readily obtained from the experimental data. The use of this small-cone method dramatically reduces the artifacts for all the data sets obtained.

With this small-cone method, we found interesting results for additional systems. In Si(111)\(\sqrt{3}\times\sqrt{3}\)-Ga, the image reveals that the Ga atoms also occupy the T4 site. The image for the Si(111)1x1 - As structure shows that the As atoms substitute for the top layer Si atoms. The result for the more complicated structure Si(100)1x2 - As clearly shows the adatom dimer. This image is the first obtained for a two-site structure. The atomic position values obtained from this small-cone method are very close to those obtained from theoretical calculations and other experimental methods, i.e., the LEED method, the x-ray standing wave method, and the grazing incidence x-ray diffraction method. The maximum discrepancy is about 0.2 Å.
DIRECT DETERMINATION OF ADSORBATE POSITIONS WITH
ENERGY-DEPENDENT AND ANGLE-RESOLVED
PHOTOELECTRON DIFFRACTION

by

Huasheng Wu

A thesis submitted in partial fulfillment
of the requirements for the degree
of
Doctor of Philosophy
in
Physics

MONTANA STATE UNIVERSITY
Bozeman, Montana

May, 1994
APPROVAL

of a thesis submitted by

Huasheng Wu

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate studies.

Date

Chairman, Graduate Committee

Approved for the Major Department

Date

Head, Major Department

Approved for the College of Graduate Studies

Date

Graduate Dean
STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. I further agree that copying of this thesis is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this thesis should be referred to University Microfilms International, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted: the exclusive right to reproduce and distribute copies of the dissertation in and from microfilm and the right to produce and distribute by abstract in any format.

Signature

Date may 31, 1994
ACKNOWLEDGMENT

First of all I wish to thank my advisor, Prof. Gerald J. Lapeyre. His constant strong interest and enthusiasm for the pursuit of science and his courage in exploring new scientific directions have set a wonderful example for me. I will never forget Dr. James Anderson. His patient advice and guidance made it possible for me to master the many complex techniques of surface science.

I give special thanks to Prof. S. Y. Tong and Dr. H. Huang in Univ. of Wisconsin-Milwaukee for many of their theoretical consultations. I am grateful to Professor John Hermanson for his encouragement of my research and to Dr. Recep Avcı for his experimental consultations. I express my deep gratitude to Dr. Cliff Olson at the Wisconsin Synchrotron Radiation Center (SRC) for much valuable advice regarding the beam line and other experimental techniques.

I also appreciate the great help of electronic technician Erik Andersen and machinist Norman Williams in the construction, and repair of the experimental apparatus. In addition, student Mickey Yu contributed a great deal in developing the experimental hardware, and spent many sleepless nights and days working at the SRC. Students Lin Zhu and Jianchao Wu also helped in many ways.

Finally, half my success in completing this endeavor is attributed to my wife, Meichun Ye, whose loving care of our family gave me plenty of precious time for my study and research.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>iv</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xi</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Determination of Interface Structure</td>
<td>1</td>
</tr>
<tr>
<td>Direct Methods with Photoelectron Diffraction</td>
<td>2</td>
</tr>
<tr>
<td>Motivation and Arrangement</td>
<td>5</td>
</tr>
<tr>
<td>II. PRINCIPLE OF FULL-WINDOW TRANSFORM</td>
<td>6</td>
</tr>
<tr>
<td>Photoelectron Diffraction</td>
<td>6</td>
</tr>
<tr>
<td>Photoexcitation Distribution and Atomic Scattering Factor</td>
<td>7</td>
</tr>
<tr>
<td>Photoelectron Diffraction Intensity</td>
<td>11</td>
</tr>
<tr>
<td>Full-Window Transform</td>
<td>12</td>
</tr>
<tr>
<td>Single Energy Holograph</td>
<td>12</td>
</tr>
<tr>
<td>Full-Window Transform</td>
<td>13</td>
</tr>
<tr>
<td>Effect of Multiple Scattering</td>
<td>15</td>
</tr>
<tr>
<td>III. IMPLEMENTATION OF FULL-WINDOW TRANSFORM</td>
<td>17</td>
</tr>
<tr>
<td>Synchrotron Radiation and Monochromators</td>
<td>17</td>
</tr>
<tr>
<td>Vacuum Chambers and Controllers</td>
<td>23</td>
</tr>
<tr>
<td>Alignment Procedures</td>
<td>28</td>
</tr>
<tr>
<td>Data Acquisition Procedures</td>
<td>31</td>
</tr>
<tr>
<td>Data Analysis Procedures</td>
<td>34</td>
</tr>
</tbody>
</table>
Results for Si(111)\(\sqrt{3}\times\sqrt{3}\)-Al ................................. 37

IV. SMALL-CONE METHOD ................................................................. 48
   Deficiency of the Full-Window Transform ................................. 48
   Small Window Behavior of the CIS Inversion ............................. 52
      Experimental Observation .................................................. 52
      Theoretical Analysis ....................................................... 55
   Sources of Artifacts within Full-Window Transform ............... 57
   Small-Cone Method ............................................................... 58
   Implementation of Small-Cone Method ................................. 60
      Inner Potential Correction ............................................... 60
      Making \(\chi\) Continuous .................................................. 61
      CIS Choice in a Small Cone ............................................ 62
      Phase Shift Correction ................................................... 63

V. RESULTS FROM SMALL-CONE METHOD .............................................. 65

   Si(111)\(\sqrt{3}\times\sqrt{3}\)-Al ..................................................... 66
   Si(111)\(\sqrt{3}\times\sqrt{3}\)-Ga .................................................. 74
   Si(111)1x1-As ................................................................. 83
   Si(100)1x2-As ................................................................. 90

VI. DISCUSSION AND CONCLUSIONS ............................................. 104

   Comparison of Related Methods ......................................... 104
   Conclusions ................................................................. 109

APPENDICES ....................................................................................... 112
   A. Adjustment of the Hemispherical Analyzer ...................... 113
   B. Effect of the Small-Cone Width .................................. 117

REFERENCES ...................................................................................... 126
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Comparison of Atomic Positions for Si(111)$\sqrt{3}\times\sqrt{3}$-Al From Full-Window Transform and From the LEED I-V</td>
<td>41</td>
</tr>
<tr>
<td>2. Comparison of Atomic Positions for Si(111)$\sqrt{3}\times\sqrt{3}$-Al From Small-Cone Method and From the LEED I-V, Calculation</td>
<td>74</td>
</tr>
<tr>
<td>3. Comparison of Atomic Positions for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga From Small-Cone Method and From the LEED I-V</td>
<td>82</td>
</tr>
<tr>
<td>4. Comparison of Atomic Positions for Si(111)1x2-As From Small-Cone Method and From the LEED I-V, XSW, GIXD, Calculation</td>
<td>101</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Photoemission Process</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Photoelectron Diffraction Phenomenon</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>Photoelectron Diffraction</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>CIS Inversions from 3 Hypothetical CIS's</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>Synchrotron Radiation Storage Ring</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>Synchrotron Radiation Spectrum in the Wisconsin SRC</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>Montana/Iowa Beam Line Monochromators</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>Grating Dispersion</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>ERG Grating System</td>
<td>21</td>
</tr>
<tr>
<td>10</td>
<td>Photon Flux vs. Photon Energy for the 2 m ERG</td>
<td>23</td>
</tr>
<tr>
<td>11</td>
<td>Vacuum Chamber Set Up</td>
<td>24</td>
</tr>
<tr>
<td>12</td>
<td>Sample and Manipulator Combination</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>Goniometer (a) and Hemispherical Analyzer (b)</td>
<td>26</td>
</tr>
<tr>
<td>14</td>
<td>Fine Alignment Procedures</td>
<td>29</td>
</tr>
<tr>
<td>15</td>
<td>Measurement Geometry</td>
<td>30</td>
</tr>
<tr>
<td>16</td>
<td>Data Acquisition Procedures</td>
<td>32</td>
</tr>
<tr>
<td>17</td>
<td>Choice for Set of Emission Directions</td>
<td>33</td>
</tr>
</tbody>
</table>
18. A Typical EDC, CIS, $I_0(k)$ and $\chi$ for Si(111)$\sqrt{3}\times\sqrt{3}$-Al ......................... 36
19. LEED Pattern (a) and Wide-Scan EDC (b) for Si(111)$\sqrt{3}\times\sqrt{3}$-Al ..................... 38
20. Representative CIS's for Si(111)$\sqrt{3}\times\sqrt{3}$-Al .................................................. 39
21. A CIS Inversion from Si(111)$\sqrt{3}\times\sqrt{3}$-Al Experimental Data ............................ 42
22. (a)-(d) Atomic Images for Si(111)$\sqrt{3}\times\sqrt{3}$-Al from Full-Window Transform .......... 43-46
23. Si(111) Surface Structure Model ...................................................................................... 47
24. Atomic Images for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga (a) & (b) and for Si(111)1x1-As (c)
From Full-Window Transform ......................................................................................... 49-51
25. Angular Dependence of the Phase and Amplitude of CIS Inversion for
Si Atom D (a) & (b) and Atom A (c) & (d) for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga ......................... 53-54
26. Small-Cone Method ........................................................................................................... 58
27. Inner Potential Effect ........................................................................................................ 60
28. Angular Dependence of the Phase and Amplitude of CIS Inversion for
Si Atom A (a) & (b) and Atom D (c) & (d) for Si(111)$\sqrt{3}\times\sqrt{3}$-Al .............................. 67-68
29. (a)-(e) Atomic Images for Si(111)$\sqrt{3}\times\sqrt{3}$-Al from Small-Cone Method .................. 69-73
30. Wide-Scan EDC (a) and Representative CIS's (b) for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga ............... 75-76
31. (a)-(e) Atomic Images for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga from Small-Cone Method ................. 77-81
32. Wide-Scan EDC (a) and Representative CIS's (b) for Si(111)1x1-As ......................... 84-85
33. (a)-(b) Angular Dependence of the Phase and Amplitude of CIS Inversion
for Si Atom D for Si(111)1x1-As ...................................................................................... 86
34. (a)-(c) Atomic Images for Si(111)1x1-As from Small-Cone Method ............................... 87-89
35. Si(100) 4° 2x1 Single Domain Structure (a)
and Representative CIS's for Si(100)1x2-As (b) ............................................................... 92-93
36. (a)-(b) Angular Dependence of the Phase and Amplitude of CIS Inversion
for Si Atom A for Si(100)1x2-As ...................................................................................... 94
37. (a)-(d) Atomic Images for Si(100)1x2-As from Small-Cone Method ..........96-99

38. (a) Effective System for Si(100)1x2-As When Put Two Emitters Together
    (b) Projection of 30 Paraboloids in the Top As Plane ...................... 102-103

39. Contour Plots of the Atomic Images for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga (a)
    and for Si(111)$\sqrt{3}\times\sqrt{3}$-Al (b) from Pathlength Method ............ 105-106

40. Schematic Comparison of Related Methods ........................................... 108

41. Adjustment of the Hemispherical Analyzer ......................................... 115

42. (a)-(g) Vertical Planar Cut of the Image Function for
    Si(111)$\sqrt{3}\times\sqrt{3}$-Ga with Different Cone-Width ..................... 119-125
ABSTRACT

The atomic structure of an interface governs most properties of the interface. For the first time, we successfully implemented a method to directly determine the adsorbate positions using energy-dependent and angle-resolved photoelectron diffraction. This method inverts the energy-dependent diffraction curves to 3-D real space, and then sums the results over all the emission directions to obtain the atomic image. The result for Si(111)\(\sqrt{3}\times\sqrt{3}\)-Al clearly shows the Si atoms around the emitter Al and identifies the Al as occupying the T4 site. This is the best atomic image ever published, with no twin image and with good atomic position values.

To further reduce the artifacts associated with this method, the angle dependence of the effective scattering factor was examined. The result suggests that the artifacts are from the large phase variation of this factor when the emission directions are far away from the emitter-scatterer direction. As a consequence, we introduced a new transform scheme - the small-cone method. To calculate the image function intensity at a given position vector in real space, we now use only those diffraction curves with their emission directions within a small cone, the axis of which is opposite to the given position vector. The width of the small cone can be readily obtained from the experimental data. The use of this small-cone method dramatically reduces the artifacts for all the data sets obtained.

With this small-cone method, we found interesting results for additional systems. In Si(111)\(\sqrt{3}\times\sqrt{3}\)-Ga, the image reveals that the Ga atoms also occupy the T4 site. The image for the Si(111)1x1 - As structure shows that the As atoms substitute for the top layer Si atoms. The result for the more complicated structure Si(100)1x2 - As clearly shows the adatom dimer. This image is the first obtained for a two-site structure. The atomic position values obtained from this small-cone method are very close to those obtained from theoretical calculations and other experimental methods, i.e., the LEED method, the x-ray standing wave method, and the grazing incidence x-ray diffraction method. The maximum discrepancy is about 0.2 Å.
CHAPTER I

INTRODUCTION

Determination of Interface Structure

The atomic structure of an adatom layer governs most properties of the interface, and therefore structure determination has involved tremendous efforts and many different methods have been devised to achieve answers. Basically, the methods can be divided into two groups according to the way they approach the problems. One is the trial and error approach, such as the low energy electron diffraction intensity-voltage curve (LEED I-V) method [1] and the x-ray photoelectron diffraction (XPD) [2] method, in which the experimental data are fitted to theoretical simulations based on trial structure models with many parameters so as to obtain a most favorable structure from the best fit. If the models are good, this approach can reach an accuracy of about 0.02 Å. However, a serious defect of this approach is that the results obtained are model dependent. To avoid this problem, a second approach is used involving the direct calculation of the atomic structure from the experimental data. The first direct method to be developed was extended x-ray absorption fine structure (EXAFS)[3], followed by surface EXAFS [4].
which provides a scalar distance - the bond length. Then another powerful tool - scanning tunneling microscopy (STM)[5] was developed, which gives a two-dimensional atomic resolution pattern for a surface. Of course the new uses of x-ray scattering are finding important applications [6]. However, the direct determination of three-dimensional atomic structure did not begin until the late 1980's, with the use of photoelectron diffraction.

Direct Methods with Photoelectron Diffraction

The phenomenon of photoelectron diffraction has been known since the 1970's. The incident photon with energy $hv$ generates photoelectron with kinetic energy $E_k = hv - E_b - W$ from the core level with binding energy $E_b$ in the sample with work function $W$, as is shown in Fig. 1. The intensity of the core-level emission peak is generally a strong function of the emission direction and the kinetic energy of the photoelectron as the result of photoelectron diffraction. This phenomenon results from the interference of the electron wave propagating directly away from the emitting atom (emitter), and the wave scattered by the neighboring atoms (scatterers), as shown in Fig. 2.

In 1986, A. Szoke [7] pointed out that the photoelectron diffraction pattern can be viewed as a hologram. The direct wave serves as the reference wave, and the scattered wave as the object wave. The positions of the scatterers relative to the emitter can be obtained by transforming the diffraction pattern over the emission direction (referred to as
Figure 1. Photoemission Process

Figure 2. Photoelectron Diffraction Phenomenon
single-energy holography (SEH)). Two years later, J. J. Barton [8] formalized Szoke's idea and did computer simulations to demonstrate the potential of this method. The first experimental result was reported in 1990 by B. Tonner and his group[9] for Cu(100), which indeed reveals the three-dimensional atomic structure. Since then, quite a few computer simulations and some experiments have been carried out [10-13]. Unfortunately, all the atomic images exhibit some serious problems: a twin image (strong intensity at the position inverted about the origin from the real atom position), a large position shift from the real atom position (at least 1 Å shift in radial direction) and significant artifacts (false indication of the possible presence of atoms). To overcome these problems, in 1991, J. J. Barton [14] suggested multiple-energy holography, which phase sums result from several single energy holograms. The experimental result by L. J. Terminello[15] in 1992 shows much improved atomic images.

To make full use of the potential of photoelectron diffraction, in July 1992, S. Y. Tong et al. proposed another approach [16]. In this method, the energy-dependent diffraction curves are obtained by measuring the photoemission peak intensity at many photon energies and at a set of emission angles which form a grid over the emission hemisphere. Each energy-dependent curve, which is a generalized Constant Initial State spectrum (thus it will be referred to as CIS later) [17,18], is inverted by transforming over the energy (wave number). Finally, the results from all CIS's are summed point-by-point in real space (this is referred to as a full-window transform) to obtain the image function. Mathematically, this method can get rid of the twin image and give much more accurate atomic positions and smaller artifacts.
Motivation and Arrangement

It is the purpose of this work to experimentally implement and improve the method advanced by S. Y. Tong *et al* and apply it to several important interface systems.

The rest of the chapters are arranged as following. Chapter 2 describes the principle of the full-window transform based on the theory of photoelectron diffraction. Chapter 3 deals with the detailed experimental equipment, procedures, data analysis and presents the first successful result for Si(111)$\sqrt{3}\times\sqrt{3}$-Al. Chapter 4 reveals and analyzes the difficulties that are inherent in the full-window transform and presents the small-cone method which overcomes those difficulties. Chapter 5 displays all results from the small-cone method. Chapter 6, the last chapter, compares the method with other related methods, and summarizes this work.
CHAPTER II

PRINCIPLE OF FULL-WINDOW TRANSFORM

Photoelectron Diffraction

A polarized photon with energy $hv$ ejects a photoelectron from the emitter with a certain angular distribution $F(\hat{k}, k)$, with $\hat{k}$ and $k$ the direction and the magnitude of the electron momentum, respectively. Part of the electron wave goes directly to the detector as the reference wave $\psi_R$. Other part of the electron wave is scattered by the scatterers located at position $r_j$ ($j=1,2,...$) with atomic scattering factor $f(\hat{k} \cdot \hat{r}_j, k)$, then goes to

Figure 3. Photoelectron Diffraction.
the detector as the object wave \( \psi_0 \). These waves interfere with each other to form a diffraction pattern \( I(k) \) at the detector which is located away from the sample with a macroscopic distance \( D \). See Fig. 3.

Actually there are many emitters involved. However, the electron waves from the different emitters are incoherent due to the inelastic nature of the photoexcitation. The signals from all the emitters are simply added together.

**Photoexcitation Distribution and Atomic Scattering Factor**

The interaction between the photoelectron and the incident electromagnetic field with vector potential \( \mathbf{A} \) is described by following Hamiltonian [19]:

\[
H = \frac{1}{2m} \left( \mathbf{p} - \frac{e}{c} \mathbf{A}(\mathbf{r},t) \right)^2 + V(\mathbf{r}) = H_0 + H_1 + H_2, \tag{1}
\]

with \( V(\mathbf{r}) \) the electric potential at the emitter atom, and \( H_0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \), the unperturbed Hamiltonian.

Also, \( H_1 = -\frac{e}{2mc} [\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}] \) is the first-order perturbation Hamiltonian, with \( H_2 \) negligible.

Noting that \( \mathbf{p} \cdot \mathbf{A} \psi = \hbar \nabla \cdot (\mathbf{A} \psi) = \hbar \left[ \psi (\nabla \cdot \mathbf{A}) + (\mathbf{A} \cdot \nabla) \psi \right] \), and choosing the Coulomb gauge \( \nabla \cdot \mathbf{A} = 0 \), we obtain: \( \mathbf{p} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{p} \),

or: \( H_1 = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} \). \( \tag{2} \)
For a plane electromagnetic wave with angular frequency $\omega=2\pi v$ and propagation vector $\mathbf{K}$, the vector potential $\mathbf{A}$ takes the form:

$$\mathbf{A}(\mathbf{r},t) = \mathbf{e} \exp[i(\mathbf{K} \cdot \mathbf{r} - \omega t)]$$

with $\mathbf{e}$ the polarization vector. In our photoemission experiment, $r \sim a_0$, the Bohr radius; and the wave-length $\lambda > 30\AA$, which leads to $Kr \sim a_0 \sqrt{\lambda} << 1$. Using the so-called dipole approximation $\exp(i\mathbf{K} \cdot \mathbf{r}) \sim 1$, Eq. (2) can be written as

$$H_1 = -\frac{e}{mc} \mathbf{e} \cdot \mathbf{p} \mathbf{e}^{i \omega t}. \quad (4)$$

Using the first-order perturbation theory of quantum physics, the transitions governed by the interaction Hamiltonian Eq. (4) between two eigenstates of $H_0$, the initial state $|i\rangle$ with energy $E_i$ and the final state $|f\rangle$ with energy $E_f$, obey energy conservation $E_f - E_i = \hbar \omega$, and the matrix element for the transition is proportional to $<f|e.p|i>$. Then using the commutation rule: $\mathbf{p} = -i\hbar [H_0, \mathbf{r}]$, the transition matrix element can be written as

$$<f|e.p|i> \sim <f|e.[H_0, \mathbf{r}]H_0|i> = (E_f - E_i) <f|e.r|i> \quad (5)$$

Taking the polarization direction $\mathbf{e}$ as the $z$ direction, the transition matrix element can be further written as

$$<f|e.r|i> \sim <f|\mathbf{r}.Y_{10}|i>, \quad (6)$$

with $Y$ the spherical harmonic.

The initial state for core level emission can be written as [16]
\[ |i> = R_{n,l_0,m_0}> \tag{7} \]

with \( n \) the principle quantum number, and \( l_0 \) and \( m_0 \) the angular momentum quantum numbers.

The final state, usually a continuum state, has the asymptotic form of a plane wave plus an incoming spherical wave, and can be written as

\[ <f| = 4\pi \sum_{l_0} (i) l e^{-i\delta_l} Y_{lm}^* (\hat{k}) Y_{lm} (\hat{r}) R_{kl} (r) / kr. \tag{8} \]

The \( \delta_l \) is the phase shift of the \( l \)th partial scattering wave, and \( R_{kl}(r) \) is the solution of the following radial equation:

\[ \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d}{dr} R_{kl} (r) \right] + \left[ k^2 - \frac{l(l + 1)}{r^2} - \frac{2m}{\hbar^2} V(r) \right] R_{kl} (r) = 0, \tag{9} \]

and which satisfies the asymptotic behavior

\[ R_{kl} (r) \xrightarrow{kr \to \infty} \frac{1}{kr} \sin(kr - \frac{l\pi}{2} + \delta_l). \tag{10} \]

Putting Eq. (7) and (8) into Eq. (6), we obtain the photoexcitation angular distribution as:

\[ F(\hat{k},k) = <f| \mathbf{e} \cdot \mathbf{r}|i> = \sum_{lm} a_{lm} (k) Y_{lm}^* (\hat{k}), \tag{11} \]

with \( a_{lm} (k) = \frac{4\pi}{k} i^l e^{-i\delta_l} <lm|Y_{l_0} l_0 m_0> \int_0^\infty R_{nl_0} (r) R_{kl} (r) dr. \tag{12} \]
From the orthogonality properties of spherical harmonics, the transition selection rules are:

\[ l = l_0 \pm 1, \ m = m_0. \]  

(13)

As an example, if the initial state is an s orbit, with \( l_0 = 0 \) and \( m_0 = 0 \), then there is only one allowed final state: \( l = 1 \) and \( m = 0 \). In this case, we have

\[ F(k, \theta) = a_{10}(k) Y_{10}^*(\hat{k}) \propto \cos(\theta). \]  

(14)

This angular dependence of an s orbit is well known [21]. If the initial orbit is not s-like orbit, the photoexcitation angular distribution will have many complex terms (see Eq. 11). As for the atomic scattering factor, at low kinetic energy (<500 ev), it can be written as [22]:

\[ f(\hat{k}, \hat{r}, k) = f(\cos(\theta), k) \]

\[ = \frac{1}{k} \sum_{l=0}^{\infty} (2l + 1) e^{-i\delta_l} \sin(\delta_l) P_l(\cos(\theta)), \]  

(15)

where \( \theta \) is the scattering angle, and \( P_l \) is the Legendre polynomial. \( \delta_l \), the phase shift of the \( l \)th partial scattering wave, comes from Eqs. (9) and (10) with \( v(r) \) the electric potential around the scatterer.
Photoelectron Diffraction Intensity

In Fig. 3, taking the emitter position as the origin and considering only single scattering events, the reference wave $\psi_R$ and the object wave $\psi_o$ can be written as:

$$\psi_R(k) = F(\hat{k}, k) \frac{e^{ikD}}{D}, \quad (16)$$

$$\psi_o(k) = \sum_j F(\hat{r}_j, k) \frac{e^{ikr_j}}{r_j} f(\hat{r}_j \cdot \hat{k}, k) e^{ikr_j} \frac{e^{ikD}}{D} e^{-\gamma l_j}$$

$$= \psi_R \sum_j A(k, r_j) e^{i(kr_j - kr)} , \quad (17)$$

with $A(k, r_j) = F(\hat{r}_j, k) F^{-1}(\hat{k}, k) f(\hat{r}_j \cdot \hat{k}, k) \frac{e^{-\gamma l_j}}{r_j}. \quad (18)$

$A(k, r_j)$ can be called as the effective scattering factor. The factor $e^{-\gamma l_j}$ accounts for the inelastic scattering of the photoelectron, where $l_j$ is the distance traveled inside the sample, and $\gamma$ is the attenuation coefficient.

The photoelectron diffraction intensity $I(k)$ and its normalized intensity $\chi(k)$ obey the relations:

$$I(k) = (\psi_R + \psi_o) (\psi_R + \psi_o)^* = |\psi_R|^2 (1 + \chi(k)), \quad (19)$$

$$\chi(k) = I(k) / |\psi_R|^2 - 1$$

$$= \sum_j A(k, r_j) e^{i(kr_j - kr)} + \sum_j A^*(k, r_j) e^{-i(kr_j - kr)}$$

$$+ \sum_j \sum_l A(k, r_j) A^*(k, r_l) e^{i(kr_j - kr_l) - (kr_j - kr)} . \quad (20)$$
These equations show that the diffraction intensity is a function of both the direction $\hat{k}$ and the magnitude $k$ of the electron momentum. Usually $|A|<1$, which implies that the single summation terms in Eq. (20) dominate the normalized intensity. As a consequence only the single summation terms will be considered in this chapter.

**Full-Window Transform**

**Single-Energy Holography**

It is informative to become acquainted with the so-called single-energy holography before we introduce the full-window transform. By measuring a diffraction pattern as a function of the emission direction $\hat{k}$ at a fixed kinetic energy (or fixed magnitude $k$) and then transforming it over the direction with the following formula, one obtains the single-energy holographic intensity[8]:

$$U(R) = \left| \int \chi(\hat{k}, k)e^{ikR}d\hat{k} \right|^2,$$  \hspace{1cm} (21)

where $R$ is the real-space variable. Putting the general expression of $\chi(k)$, Eq. (20), with only the single summation terms, into Eq. (21), we can predict the result:

$$U(R) = \left| \sum_j \int A(k, r_j)e^{ikr_j}e^{ik(R-r_j)}d\hat{k} + \sum_j \int A^*(k, r_j)e^{-ikr_j}e^{ik(R+r_j)}d\hat{k} \right|^2.$$  \hspace{1cm} (22)
It is clear that when $R = \pm r_j$, $U(R)$ will have maximum intensity. That means the image function Eq. (22) will have a large intensity at the actual atomic position $r_j$ as well as at the inverted position $-r_j$, which gives the so-called twin image.

**Full-Window Transform**

In contrast with the single-energy holography, the full-window transform of S. Y. Tong et al [16] uses energy-dependent and angle-resolved diffraction data and takes two steps for the transform. The first step inverts the energy-dependent diffraction curve (CIS) taken in the direction $\hat{k}$, $\chi(\hat{k}, k)$, to the CIS inversion:

$$\Phi(\hat{k}, R) = \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(\hat{k}, k) e^{-i k \cdot R} g(k) dk,$$

with $g(k)$ a smooth window function introduced to reduce artificial oscillations in the inverted function. Putting the general expression of the normalized diffraction intensity, Eq. (20), into the above equation, one obtains:

$$\Phi(\hat{k}, R) = \sum_j \int_{k_{\text{min}}}^{k_{\text{max}}} A(k, r_j) e^{-i k \cdot R \cdot (1 - \hat{k} \cdot \hat{r_j})} g(k) dk$$

$$+ \sum_j \int_{k_{\text{min}}}^{k_{\text{max}}} A^*(k, r_j) e^{-i k \cdot R \cdot (1 - \hat{k} \cdot \hat{r_j})} g(k) dk.$$  

(24)

The CIS inversion $\Phi(\hat{k}, R)$ gets maximum amplitude from the first term in Eq. (24) when

$$R(1 - \hat{k} \cdot \hat{R}) = r_j (1 - \hat{k} \cdot \hat{r}_j).$$

(25)
Since in this case, $\mathbf{k}$ and $\mathbf{r}_j$ are fixed, Eq. (25) can be written as:

$$R = \frac{\text{Constant}}{1 - \cos(\theta_R)},$$

(26)

with $\theta_R$ the angle between the vector $\mathbf{R}$ and the direction $\mathbf{k}$. This is a standard formula for a paraboloid of revolution with $\mathbf{k}$ as its rotation axis. In particular, this paraboloid passes through the scatterer position $\mathbf{R}=\mathbf{r}_j$, which does not depend on the emission direction $\mathbf{k}$. The corresponding complex value on the paraboloid is simply (see Eq. (24)):

$$\Phi(\mathbf{k},\mathbf{r}_j) = \int_{k_{\text{min}}}^{k_{\text{max}}} A(\mathbf{k},\mathbf{r}_j) g(k) \, dk = A(\mathbf{k},\mathbf{r}_j) (k_{\text{max}} - k_{\text{min}}).$$

(27)

This value is now only a function of the CIS direction $\mathbf{k}$ and is proportional to the momentum-averaged effective scattering factor, $\overline{A(\mathbf{k},\mathbf{r}_j)}$. It is constant everywhere on the paraboloid. The CIS inversion $\Phi(\mathbf{k},\mathbf{R})$ does not have maximum amplitude at any position from the second term in Eq. (24), because both $(1 - \mathbf{k} \cdot \mathbf{R})$ and $(1 - \mathbf{k} \cdot \mathbf{r}_j)$ are positive, and $\mathbf{R}$ and $\mathbf{r}_j$ should be positive too. With this transform, therefore, we eliminate the problem of twin images which is inherent in the single-energy holography. Figure 4 shows three CIS inversions $\Phi(\mathbf{k},\mathbf{R})$ which are inverted from hypothetical CIS's in the direction $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3$ respectively.

The second step of the full-window transform sums the CIS inversions $\Phi(\mathbf{k},\mathbf{R})$ over all emission directions $\mathbf{k}$ to obtain the image function (and this is the reason that this method is referred to as the full-window transform):

$$U(\mathbf{R}) = \left| \sum_{\text{all } \mathbf{k}} \Phi(\mathbf{k},\mathbf{R}) \right|^2.$$

(28)
Since all paraboloids pass through the jth atom $\mathbf{R} = \mathbf{r}_j$, $U(\mathbf{R})$ would have a large intensity at $\mathbf{R} = \mathbf{r}_j$, if all $\Phi(\hat{k}, \mathbf{r}_j)$'s are in phase at $\mathbf{R} = \mathbf{r}_j$.

Figure 4. CIS inversions from CIS's with different emission directions

Effect of Multiple Scattering

Generally, photoelectrons undergo both single scattering and multiple scattering, the simplest form of which is double scattering. Double scattering refers to the event where an electron is first scattered by a scatterer at the position $\mathbf{r}_i$, relative to the emitter, then it is scattered by a second scatterer at the position $\mathbf{r}_j$, and finally goes to the detector. The corresponding normalized diffraction intensity for this double scattering event is (refer to Fig. 3) [16]:

$$\chi_{\text{double}}(\hat{k}, k) = \sum_i \sum_j B(k_i, \mathbf{r}_i, \mathbf{r}_j) e^{i(k_i + |\mathbf{r}_i| - \mathbf{r}_j - \mathbf{r}_j - \mathbf{k}_r)}.$$ (29)
Substituting Eq. (29) into Eq. (23), the CIS inversion $\Phi(\hat{k}, R)$ will have maximum amplitude on the new paraboloid which satisfies the condition:

$$R - k \cdot R = (r_i + |r_j - r_i|) - k \cdot r_j.$$ \hspace{1cm} (30)

However, unlike the single-scattering case (see Eq. (25)), Eq. (30) does not have a $\hat{k}$-independent solution for $R$. That means the maximum-amplitude paraboloids formed from the double scattering events (and generally from the multiple-scattering events) do not intersect at a common point. Therefore after the summation of $\Phi(\hat{k}, R)$ using Eq. (28), the multiple scattering contribute only to the background.
CHAPTER III

IMPLEMENTATION OF FULL-WINDOW TRANSFORM

Synchrotron Radiation and Monochromators

Figure 5. Schematic drawing of synchrotron radiation storage ring
All experiments were carried out at the Wisconsin Synchrotron Radiation Center. A schematic drawing of the Wisconsin storage ring is shown in Fig. 5. Electrons generated from tungsten filaments are accelerated to about 100 MeV in the microtron, then injected in 15 small bunches into the electron storage ring which has a circumference of about 88 m. The electrons move around the storage ring with a period of about 300 ns corresponding to a speed very close to the speed of light. When they are bent by the bending magnets, the electrons radiate electromagnetic waves which are highly concentrated in the tangential direction (the beam line direction) with a polarization parallel to the plane of the orbit. The continuous spectrum covers the range from infrared
to about 3 keV (or 5 keV) for an electron energy of 800 MeV (or 1 GeV). The photon flux as a function of photon energy for the two electron energy cases are shown in Fig. 6 [23].

Before the photon goes to the sample, its energy is selected by the monochromator. Figure 7 shows schematically the monochromators on the Montana/Iowa beam line. The radiation from the ring can go by two routes. One is directly through the Extended Range Grasshopper (ERG) monochromator which has two spherical gratings, 2 m and 5 m. In the other route, the path is bent up then down passing through the modified Seya-Nomioka monochromator with four gratings of different ruling spacings. The Seya (or ERG) monochromator can be chosen by moving the flat mirrors A and B up (or down). The different gratings can be selected manually. Both monochromators focus the beam to the same point about 25 inches beyond the end of the beam line and 50 inches above the floor.

Figure 7. Montana/Iowa beam line monochromators
The monochromator chooses a wavelength $\lambda$ (or photon energy $h\nu$) by changing the incident angle $\alpha$ and the exit angle $\beta$ at the grating, as is shown in Fig. 8. The equations governing the process are [24]:

$$m\lambda = d (\sin(\alpha) - \sin(\beta)), \quad (m: \text{any integers})$$

$$h\nu = \frac{hc}{\lambda},$$

with $d$ the ruling spacing of the grating. Usually, $m=1$ is used for the selection of the photon energy $h\nu$.

![Grating dispersion](image)

**Figure 8. Grating dispersion**

In the case of the Seya, the position of the entrance and exit slits are fixed (see Fig. 7), so $\alpha + \beta = 2c$, with $c=35^\circ 15'$. Then,

$$\lambda = 2d \cos(c) \sin(\alpha - c).$$
The wavelength is then determined only by the incident angle, which can be changed by the rotation of the grating. When $\alpha = \beta = c$, then $m$ is zero which corresponds to specular reflection of the entire beam (the white light).

Figure 9. Grating system in ERG. The entrance slit, exit slit, and the grating are constrained on a Rowland circle. $R$ is the curvature of the grating.

In the case of the ERG, the entrance slit and the grating move together along the beam line direction, and they also rotate through different angles to constrain themselves and the position-fixed exit slit to remain on the Rowland circle, which has a diameter $R$, the curvature of the spherical grating [25]. The geometry is shown in Fig. 9. Note that $\phi_1 = 2(90^\circ - \alpha)$, $\phi_2 = 2(90^\circ - \beta)$, and $L = 2r \sin((\phi_1 + \phi_2)/2) = R \sin(\alpha + \beta)$. Let $L = L_0 + D$, with
the value of \( L \) when \( \alpha = \beta \). By solving for \( L_0 \) and \( \beta \) in terms of \( \alpha \) (a constant angle about 88°) and \( D \), and putting them into Eq. (31), one then obtains:

\[
\lambda = d \left\{ \sin(\alpha) - \sin\left( \sin^{-1}\left( \frac{D}{R} + \sin(2\alpha) \right) \right) - \alpha \right\}. \tag{34}
\]

The wavelength is then determined only by \( D \), the displacement of the grating away from the white-light position.

Both values of \( \alpha \) in the Seya and of \( D \) in the ERG can be read into the computer to calculate the photon energy or can be controlled by the computer through a stepping motor on the monochromators.

The photon energy range covered by the four gratings in the Seya is about 6–45 eV, which is suitable for the measurement of the valence band. The photon energy range from the 2 m grating in the ERG is about 40–240 eV. The photon intensity as a function of the photon energy is shown in Fig. 10. The 5 m grating in the ERG gives a photon energy range of about 300–1200 eV with a photon intensity about one tenth that from the 2 m grating.

The resolution of a monochromator depends on the monochromator type, the grating, the photon energy and the slit width. For the Seya and ERG, the resolution can be roughly written as [26]:

\[
\text{Resolution (mv)} = a \left( \frac{h \nu (eV)}{\text{ slit_width (\mu)}} \right)^2
\]

with

\[
a \left( \frac{\text{mv}}{(eV)^2/\mu} \right) = 6 \times 10^{-3} \quad \text{for the Seya}
\]

\[
= 3 \times 10^{-4} \quad \text{for the 2 m ERG}
\]

\[
= 1 \times 10^{-4} \quad \text{for the 5 m ERG.}
\]
Figure 10. Photon flux vs. photon energy for the 2 meter grating in the ERG monochromator of Montana/Iowa bean line.

Vacuum Chambers and Controllers

The vacuum chambers and controllers are shown schematically in Fig. 11. There are three chambers: the introduction chamber (3) for sample loading from air, the middle chamber (2) for sample preparation, and the analysis chamber (1) which directly connects to the monochromator chamber (26). The gate valves and angle valve (18), (19) and (30) control the passage between the chambers. The transfer manipulator (5) transfers the sample between the introduction and the middle chambers; while the transfer manipulator (4) transfers the sample between the middle and the analysis chambers. All transfers have
wobble sticks, which can rotate and move linearly to effect the sample transfer (not shown in the drawing).

The analysis chamber sits on three fine-adjustable supports (not shown in the drawing) and is pumped down by the ion pump (8), the turbomolecular pump (6), the mechanical pump (7) and the titanium sublimation pump (9).

The sample and the manipulator combination (14) is shown in more detail in Fig. 12. The sample (14a) is mounted on the transfer block (14b). The block is on the rotatable support (14c) which is coaxial with the sample normal. The manipulator (14d) can translate in the x, y, z directions and rotate about the z axis. The sample can be heated resistively by passing a current through it.

The hemispherical analyzer (HA) and the goniometer combination (11) is shown in more detail in Fig. 13(a). The analyzer (11a) moves along the circular track (11b) which is fixed on the turntable (11c). The axis of the circular track intersects the axis of the turntable perpendicularly at a point which serves the rotation center of the goniometer. Fig. 13 (b) shows the structure of the hemispherical analyzer. Electrons from
Figure 13. (a) Hemispherical analyzer and goniometer combination 11. 11a. Analyzer. 11b. Circular track. 11c. Turntable.

Figure 13. (b) Hemispherical analyzer 11a.
the sample are accelerated or retarded by the ramping voltage on the lens system to the pass-energy, which is the potential on the entrance slit. They are then deflected through the hemispheres with the help of the potentials on the inner and outer hemispheres, then strike the channeltron, where they generate many secondary electrons with the help of the high voltage [27]. The final electron pulses are amplified and counted. The mean radius of the hemisphere is 50 mm with a resolving power E/ΔE of about 100. The half acceptance angle of the analyzer is about 2°, which is very good for angle-resolved photoemission measurement.

The double-pass cylindrical mirror analyzer (CMA) (13) has a large acceptance solid angle, which is suitable for angle-integrated measurement. It can be driven in and out on a bellows. The low energy electron diffraction (LEED) system (12) is used to check the degree of order and surface symmetry structure of the sample. It can also be driven in and out. The tungsten mesh (23) is used to generate photon-electron current for data normalization. It is in the path of the incident beam and has a transmittance of about 85%. The source evaporator (17) is usually a boat or basket made of tantalum or tungsten depending on what source material being used. The quartz crystal oscillator (QCO) (16) is for the thickness monitoring of the deposition on the sample. It is put close to the sample. When the source material deposits on the sample, it also deposits onto the QCO, which increases in mass and decreases in its frequency of natural oscillation. With a careful calibration, the QCO can serve well in determining the thickness of the deposition.
Finally, the computer controls the CMA, HA controllers and accepts signal from the mesh-current amplifier, the CMA and HA signal amplifiers.

The chambers can obtain good vacuum by baking to about 140 °C for 24 hrs. The typical pressure is about $7 \times 10^{-11}$ torr in the analysis chamber, $5 \times 10^{-10}$ torr in the middle chamber, and $1 \times 10^{-6}$ torr in the introduction chamber.

**Alignment Procedures**

The most important and the most difficult part of this experiment is to set the photon beam spot on the sample surface exactly cocentral with the goniometer (the adjustment of the HA50 itself will be discussed in Appendix A).

Coarse alignment: without the other chambers, move the analysis chamber to match the marks on the frame with the marks on the floor as close as possible. Adjust the height of the three legs on the frame as marked and keep the chamber top level.

Medium fine alignment: rotate the HA to positive x direction (see Fig. 11) (with a reading of 131.8° on the turntable) and 2° downwards with the photon beam. Judge the misalignment in the y and z direction by watching the spot of white light (from the Seya) on the analyzer. Adjust the chamber to right position. Then shoot a He-Ne laser beam coaxial with the view port (10a) into the chamber. Set the sample normal about 10~15° from the white beam and move the sample to intercept both the white light and the laser beam at the sample center.
Fine alignment: set a typical photon energy and set the HA on the x-y plane and in the negative y direction (221.8° turntable reading) to get some counts from a core level emission. Change the horizontal (or vertical) deflector setting on the HA controller and watch the signal change, which indicates the misalignment in the x (or z ) direction as is shown in Fig. 14(a) and (b). Move the sample along the x direction and move the chamber along the z direction to maximize the signal counts when the deflector settings are in neutral, 5.0. Then swing the HA down by a large angle, >60°. Change the vertical deflector setting and watch the signal change, which indicates the misalignment in the y direction as is shown in Fig. 14(c). Move the chamber along the y direction to maximize the signal again. Now the photon beam passes through the center of the goniometer.

Figure 14. Fine alignment procedures. 1. Sample. 2. Beam spot on the sample. 3. Analyzer.
The next task is to set the sample normal to the desired direction which serves as the 0° of polar angle, and to set a high symmetry direction on the surface along the horizontal direction which serves as 0° of azimuthal angle.

Figure 15. Measurement geometry. (10a) and (10b) are two view ports.

Put the sample normal coaxial with the LEED (12) (see Fig. 11) and get the LEED pattern on the screen. Rotate the sample around its normal so that the LEED spots corresponding to one of the high symmetry directions lie on the horizontal direction. Write down the two angle readings from the rotating knobs (see Fig. 12): $\gamma_{\text{knob}}$ and $\phi_{\text{knob}}$. Rotate the sample to the direction shown in Fig. 15 so that the sample surface reflects the He-Ne laser beam which is coaxial with the view port (10a) to the view port (10b). The view ports (10a) and (10b) are 35° and 90° away from the beam line. So the sample normal is now 62.5° from the beam line. There is a natural mechanical coupling between the angles
γ and φ inherent in the design: when one changes γ by Δγ, the angle φ is changed automatically by Δφ=Δγ/2; but when one changes φ, the angle γ is not affected. For this reason, the angle φ now needs to be compensated back by Δφ_{knob}=-Δγ_{knob}/2. From now on, the polar angle θ is selected by the rotation of the HA in the x-y plane which contains the sample normal, the photon beam and the photon polarization vectors. And the azimuthal angle φ is selected by the rotation of the sample around its normal. Refer to Fig. 15.

**Data Acquisition Procedures**

The procedures for data acquisition are shown in diagram in Fig. 16, where all work is done automatically by computer except for the angle setting, which has to be done manually.

The emission angles (θ,φ) are chosen in one irreducible region by the sample symmetry and are so ranged that each emission direction includes about the same solid angle. For the case of Al/Si(111) system, which has three-fold rotational symmetry around the z axis and three mirror planes, the irreducible region is the region between the two adjacent mirror planes as shown in Fig. 17. Δθ is chosen to be constant and Δφ changes with θ roughly as Δφ=Δθ/sin(θ).
Figure 16. Data acquisition procedures
The photon energy $h\nu$ is chosen by keeping the momentum step $\Delta k$ a constant and according to $h\nu = E_k + \text{binding energy} + \text{work function}$, with $E_k = \frac{\hbar^2 k^2}{2m}$.

For the energy distribution curve (EDC), which is the plot of the photoelectron counts vs. its energy, the peak width increases with the photon energy because the resolution of the monochromator degrades when the photon energy increases. As a result, the EDC scans from $E_k - \text{range}/2$ to $E_k + \text{range}/2$. The range is linearly interpolated from the two measured values - range($h\nu_1$) and range($h\nu_2$), with $h\nu_1$ and $h\nu_2$ the photon energies at the two ends of the CIS. The number of steps stays the same for all EDC's, so the energy step for EDC changes corresponding to the change in the range. For each EDC, the number of scans varies to ensure that certain amount of counts are accumulated for the peak.

The photon flux, $p$, changes with energy as shown in Fig. 10 and changes with time due to the continuous loss of electrons in the storage ring. As a result, all signals which relate to the photon flux will contain this change, which makes it necessary and
useful to normalize the signal from the sample with the current from the mesh ((23) in Fig. 11). Since,

\[ I_{\text{sample}} \sim p(hv,t) (F_{\text{sample}}(hv))^2 (1+\chi(k)) T(k) \quad (\text{see Eq. (19)}) \]

and \[ I_{\text{mesh}} \sim p(hv,t) (F_{\text{mesh}}(hv))^2, \]

so \[ I_{\text{normalized}} = I_{\text{sample}} / I_{\text{mesh}} \sim (F_{\text{sample}}(hv) / F_{\text{mesh}}(hv))^2 T(k) (1+\chi(k)), \quad (36) \]

where \( T(k) \) is the transmittance of the hemispherical analyzer, which decreases smoothly with \( k \). The quantities \( F_{\text{sample}}(hv) \) and \( F_{\text{mesh}}(hv) \) are the photoexcitation cross sections for the sample and mesh respectively, which also decrease with \( hv \) smoothly in the photon energy range used in this experiment [28].

The surface quality was monitored by checking the valence band structure, which is sensitive to the oxygen and carbon contamination, every few hours. In the case of minor contamination, the sample was annealed for 30 seconds. The temperature used is about 100 °C lower than that for making the adsorbate layer.

Data Analysis Procedures

First, all EDC's are fitted with Gaussian peaks and a linear background as:

\[ I(E) = \sum_{I=1}^{n} I_I e^{-(E-E_I)/\Gamma)^2} + (A_0 + A_1 E), \quad (37) \]

where the \( I_I, E_I \) are the intensity and the peak position for \( I \)th peak and \( \Gamma \) is the peak
width. The number of peaks, \( n \), is usually 1 or 2 depending on the resolution of the EDC.

The area of the Gaussian peaks serves as the intensity \( I(k) \) which forms CIS. A non-diffractive curve \( I_0(k) \) is chosen for each CIS which corresponds to the \( k \)-dependent photoexcitation cross section and the transmittance of the analyzer (see Eq. (36)). The smooth curve, \( I_0(k) \), is generated from each CIS with a spline smooth routine in the software GENPLOT [29] and from which the normalized diffraction curve is given by \( \chi(k) = I(k)/I_0(k) - 1 \). The choice of \( I_0(k) \) affects the quality of the atomic image, but not much. In Fig. 18 is shown a representative EDC from Al 2p, fitted \( I(k) \), \( I_0(k) \) and \( \chi(k) \) from the experiment data for Al/Si(111).

The \( \chi(k) \) curves are extended over the whole emission hemisphere according to the symmetry of the sample and are transformed using Eq. (23) and (28). The window function \( g(k) \) in Eq. (23) is chosen to be the Hanning function [30] with a Hanning fraction \( h = 0.25 \):

\[
g(k) = \sin^2 \left( \frac{\pi (k - k_{\text{min}})}{2(k_2 - k_{\text{min}})} \right) \quad k_{\text{min}} < k < k_2
\]
\[
= 1 \quad k_2 < k < k_3
\]
\[
= \cos^2 \left( \frac{\pi (k - k_3)}{2(k_{\text{max}} - k_3)} \right) \quad k_3 < k < k_{\text{max}}
\]

with
\[
k_2 = k_{\text{min}} + h \left( k_{\text{max}} - k_{\text{min}} \right) / 2
\]
\[
k_3 = k_{\text{max}} - h \left( k_{\text{max}} - k_{\text{min}} \right) / 2
\]

The step size \( \Delta r \) in the real space is typically chosen to be 0.2Å.
Figure 18. Experimental Energy Distribution Curve (EDC) from Al 2p, Constant Initial State Spectrum (CIS), computer-chosen non-diffractive curve $I_0$ and normalized diffraction curve $\chi$ for Si(111)$\sqrt{3}\times\sqrt{3}$-Al.
Finally, the software - MATHEMATICA [31] is used, where a continuous function I(x,y,z) is formed from the transformed discrete data. From there all kinds of image plots are generated.

Results for Si(111)\(\sqrt{3}\times\sqrt{3})-Al [32]

The experiments were carried out in the Montana/Iowa beam line in the Wisconsin Synchrotron radiation center (SRC). The sample was prepared using standard method. The Si(111) wafer was outgassed at 500 °C for a few hours. Then it was heated to 1150 °C for 30 seconds maintaining the chamber pressure below \(1\times10^{-9}\) torr and cooled down quickly to 850 °C, then gradually cooled down to room temperature, which resulted in a good 7x7 LEED pattern and good valence band spectrum with all the surface features on. The Al was evaporated from a tantalum basket and deposited 1-2 ML (monolayers) onto the 7x7 Si surface at a rate about .5ML/min. The sample then was annealed to about 850 °C measured by an infrared pyrometer for 3 minutes, which resulted in a sharp \(\sqrt{3}\times\sqrt{3}\) LEED pattern as is shown in Fig. 19(a) with the direction choice for \(\varphi=0°\). A total of 41 CIS's were taken from the Al 2p core level emission. The angular range is 0–70° in polar angle with \(\Delta\theta=7.5°\) and 0–60° in azimuthal angle which spans between two mirror planes. For each angle, the photon energy was scanned from about 100-240 eV. The corresponding momentum range is about 3.5–7.0 (1/Å), with a constant momentum step
Figure 19. (a) Si(111)$\sqrt{3}$x$\sqrt{3}$-Al LEED pattern and the choice for $\phi$=0° (positive x direction).

Figure 19. (b) Wide-scan Energy Distribution Curve (EDC) for Si(111)$\sqrt{3}$x$\sqrt{3}$-Al.
Figure 20. Representative experimental curves $I(k)$ (CIS) (circles and solid lines) from Al 2p with computer-chosen $I_0(k)$ (dashed lines) for Si(111)$\sqrt{3}\times\sqrt{3}$-Al. The short bars on the left side are the baselines for the corresponding curves.
$\Delta k = 0.15 \text{ (1/Å). The typical energy resolution for the EDC is about } 3 \text{ eV.}$. Fig. 19(b) shows a wide-scan EDC of this system. Some representative CIS's together with the computer-chosen $I_0(k)$ are shown in Fig. 20, where the short bars on the left side indicate the base line for the corresponding curves.

In Fig. 21, a CIS inversion using Eq. (23) is shown in two-dimensional (upper panel) and three-dimensional (lower panel) for the CIS taken in the direction of $\theta = 30^\circ$, and $\phi = 180^\circ$. It shows clearly that there are two paraboloids passing through two Si atoms, which verifies the correctness of Tong's theory.

In Fig. 22(a) is shown an X-Z planar cut of the resulting image function with a cross on the origin representing the Al position. It shows that there is a Si atom on the side in the first layer and another Si atom in the second layer directly below the Al atom. The X-Y planar cuts for the first-layer and second-layer Si atoms are shown in Fig. 22(b) and (c) respectively. In Fig. 22(d) is shown a three-dimensional plot of the image function, where the Al atom is represented with the sphere O and the Si atoms A, B, C and D are plotted from the constant-intensity calculation at 60% of their maximum intensity. Comparing Fig. 22(d) with Fig. 23 which shows the clean Si(111) surface, it is clear that Al atom binds to Si atoms A, B, and C occupying the so-called $T_4$ site, which rules out another possibility that the Al binds to Si atoms A, C and H occupying the so-called $H_3$ site. This is the result that took LEED I-V method much effort. All the atomic positions are compared in Table 1 with those from LEED I-V work [33]. Good agreement is achieved, though there are artifacts of about 40% intensity here and there.
Table 1. Comparison of atomic positions for Si(111)$\sqrt{3}\times\sqrt{3}$-Al obtained from Full-Window Transform and from the LEED I-V work (Coordinate Unit: Å)

<table>
<thead>
<tr>
<th></th>
<th>$A_x$</th>
<th>$A_z$</th>
<th>OA</th>
<th>OD</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Work</td>
<td>-2.3</td>
<td>-0.8</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>LEED I-V</td>
<td>-2.1</td>
<td>-1.2</td>
<td>2.5</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Figure 21 A CIS inversion from the CIS in the emission direction of $\theta=30.0^\circ$ and $\phi=180^\circ$ for Si(111)√3×√3-Al. Coordinate Unit: Å.
Figure 22 (a) Vertical planar cut of the image functionas obtained from the full-window transform for Si(111)$\sqrt{3} \times \sqrt{3}$-Al. The cross represents the Al atom. Peaks marked A and D are due to Si atoms. Coordinate Unit: Å.
Figure 22 (b) X-Y planar cut passing through the first-layer Si atoms at $z=-0.8\text{Å}$ of the image function as obtained from the full-window transform for Si(111)$\sqrt{3}x\sqrt{3}$-Al. Coordinate Unit: Å.
Figure 22 (c) X-Y planar cut passing through the second-layer Si atoms at $z=-2.6\text{Å}$ as obtained from the full-window transform for Si(111)$\sqrt{3}\times\sqrt{3}$-Al. Coordinate Unit: Å.
Figure 22(d) Three-dimensional constant-intensity surface plot of the image function for Si(111)$\sqrt{3} \times \sqrt{3}$-Al. The Al atom is represented by the sphere O since it is the emitter. 50% of their maximum intensity is chosen for the Si atoms.
Figure 23 Si(111) surface with large, medium, small spheres represent the first-, second-, and third-layer Si atoms.
CHAPTER IV

SMALL-CONE METHOD

Deficiency of the Full-Window Transform

When the full-window transform is applied to experimental data for a new system Si(111)\(\sqrt{3}\times \sqrt{3}\)-Ga, a serious difficulty is found. Figure 24 (a) shows the X-Z planar cut of the image function for this system as obtained from the full-window transform. It shows high intensities at places like those marked A and D, which might be occupied by real atoms. However, it also shows high intensities in several other places, which by physical considerations must be artifacts of this method. Figure 24(b) shows the X-Y planar cut at the depth of the "atom" A. In addition to the larger intensity at places marked A, B, C which could be caused by real atoms, intensity peaks also appear at places close to the center, which can scarcely be attributed to real atoms. Similar artifacts are found for two other systems: Si(111)1x1-As and Si(100)1x2-As. Figure 24(c) shows the X-Z planar cut of the image function for the system Si(111)1x1-As. Besides the high intensity at location "D", significant intensities are found in other places. Such artifacts make the
Figure 24 (a) Vertical planar cut of the image function as obtained from the full-window transform for Si(111)$\sqrt{3x}\sqrt{3}$-Ga. The cross represents the Ga atom. Intensity maxima marked A and D are due to Si atoms. Coordinate Unit: Å.
Figure 24 (b) X-Y planar cut passing through the first-layer Si atoms at z=-1.2Å of the image function as obtained from the full-window transform for Si(111)$\sqrt{3}$x$\sqrt{3}$-Ga. Coordinate Unit: Å.
Figure 24 (c) Vertical planar cut of the image function as obtained from the full-window transform for Si(111)1x1-As. The cross represents the As atom. Peaks marked D is due to a Si atom. Coordinate Unit: Å.
determination of atomic position quite problematical. To overcome this problem so as to obtain high quality atomic image, the reason for the significant artifacts must be understood and a new data analysis process should be established.

Small Window Behavior of the CIS Inversion

Experimental Observation

The most important features on the image function are, of course, the features associated with real atoms. Since the intensity of the image function at the atom position $r_j$ comes from the summation of $\Phi(\hat{k}, r_j)$ (the complex CIS inversion at the position $R=r_j$) over all emission angle $\hat{k}$'s (see Eq. (28)), the direct way to understand how the full-window transform generates large artifacts on the image function is to analyze the angular behavior of $\Phi(\hat{k}, r_j)$. The dependence of $\Phi(\hat{k}, r_j)$ on the emission direction $\hat{k}$ can be obtained by transforming different CIS's to the point $R=r_j$ using Eq. (23). The atomic position $r_j$ for an unknown system can be found with a procedure which will be discussed later in this chapter.

In Figure 25(a) and (b) are shown the angular dependence of the phase and the amplitude of $\Phi(\hat{k}, r_D)$, the CIS inversions at the position of atom D in the system Si(111)$\sqrt{3}$x$\sqrt{3}$-Ga, obtained from the experimental data. The observation shows that on the emission hemisphere there exists a small angular window with a $20^\circ$ half-width. Inside the window, $\Phi(\hat{k}, r_D)$ has a relatively constant phase with a large amplitude. Outside the window $\Phi(\hat{k}, r_D)$ has a rapidly changing phase with a smaller amplitude. The center of the window is the emitter-scatterer direction, which is $\theta=0^\circ$ in this case (the structure of
Figure 25. Phase (a) and amplitude (b) of the CIS inversions at the position of Si atom D, as a function of polar angle for Si(111)$\sqrt{3} \times \sqrt{3}$-Ga. The azimuthal angles are 0° and 180° for the positive and negative polar angle values, respectively.
Figure 25. Phase (c) and amplitude (d) of the CIS inversions at the position of Si atom A, as a function of polar angle for Si(111)$\sqrt{3} \times \sqrt{3}$-Ga. The azimuthal angle is $0^\circ$. 
This system will be presented later in this chapter. This "small-window" behavior is also found for Si atom A, located at about 60° in polar angle. Figure 25(c) and (d) show the angular behavior of the phase and the amplitude of $\Phi(\mathbf{k}, \mathbf{r}_A)$. In other systems, we also found similar "small-window" behavior.

**Theoretical Analysis**

Since $\Phi(\mathbf{k}, \mathbf{r}_j)$ is proportional to the momentum-averaged effective scattering factor $A(\mathbf{k}, \mathbf{r}_j)$ (see Eq. (27)) and the effective scattering factor is composed of the atomic scattering factor $f(\mathbf{k} \cdot \mathbf{r}_j, k)$ and the photoexcitation matrix element $F(\mathbf{k}, k)$ (see Eq. (18)), the main feature of this "small-window" behavior of $\Phi(\mathbf{k}, \mathbf{r}_j)$ can be understood and therefore can be proven to be general by examining the angular dependence of $f(\mathbf{k} \cdot \mathbf{r}_j, k)$ and $F(\mathbf{k}, k)$.

The atomic scattering factor with amplitude $|f(\theta)|$ and phase shift $\Delta(\theta)$ can be written as (see Eq. (15)):

$$|f(\theta)| e^{i\Delta(\theta)} = \frac{1}{k} \sum_l (2l + 1) e^{i\delta_l} \sin(\delta_l) P_l(\cos(\theta)).$$  \hfill (40)

Taking the derivative with respect to $\theta$ on both sides of Eq. (40) and setting $\theta=\pi$, one obtains

$$|f(\pi)|=0,$$  \hfill (41a)

and

$$\Delta'(\pi)=0.$$  \hfill (41b)
Equation (41) shows that there is an angular region in the neighborhood of the $\pi$ scattering direction in which both the amplitude and phase of the atomic scattering factor are nearly unchanged with angle. Many detailed calculations using Eq. (40) give further evidence that Eq. (41a) corresponds to a local maximum [34].

Now let us rewrite the photoexcitation matrix element as (see Eq. (11)–(13)):

$$ F(\mathbf{k}, k) = \sum_{l,m} a_{lm}(k) Y_{lm}^\ast(\mathbf{k}) , \quad (l = l_0 \pm 1, \ m = m_0). $$

(42)

The $a_{lm}$ is determined by the emitter potential, the initial state $|I_0, m_0\rangle$ and the momentum of the final state. The $Y_{lm}$ are the spherical harmonics with the symmetry $Y_{lm}(-\mathbf{r}) = (-1)^l Y_{lm}(\mathbf{r})$. Within the small angular window, where $\mathbf{k} \approx -\mathbf{r}_j$,

$$ F(\mathbf{k}, k) = \sum_{l,m} a_{lm}(k) Y_{lm}^\ast(-\mathbf{r}_j) = (-1)^{l+1} \sum_{l,m} a_{lm}(k) Y_{lm}^\ast(\mathbf{r}_j) = (-1)^{l+1} F(\mathbf{r}_j, k). $$

(43)

This transforms Eq. (18) to $A(\mathbf{k}, r_j) \sim (-1)^{l+1} f(\mathbf{k} \cdot \mathbf{r}_j, k)$. That is, the behavior of $\Phi(\mathbf{k}, r_j)$ is largely determined by $f(\mathbf{k} \cdot \mathbf{r}_j, k)$ within the small window. Beyond the small window, generally, the product $F(\mathbf{r}_j, k) F^{-1}(\mathbf{k}, k)$ is not unity. Instead, the phase of this function changes rapidly with the direction $\mathbf{k}$ for non-$s$ initial states due to the multiple complex terms in Eq. (42), this is responsible for the strange phase behavior of $\Phi(\mathbf{k}, r_j)$ in this region. Also, the amplitude of this function changes with the direction $\mathbf{k}$. When $|F(\mathbf{r}_j, k) F^{-1}(\mathbf{k}, k)| \leq 1$, we have $|A(\mathbf{k}, r_j)| \leq |f(\mathbf{k} \cdot \mathbf{r}_j, k)|$, which reduces $\Phi(\mathbf{k}, r_j)$ to smaller amplitude in this region. When $|F(\mathbf{r}_j, k) F^{-1}(\mathbf{k}, k)| \gg 1$, $\chi(\mathbf{k}, k)$ in Eq. (20) is dominated by the double summation, where the condition $R=r_j$ does not
yield zero phase in the oscillatory factor, so that \( \Phi(\mathbf{k}, r_j) \) also becomes small. In this case, however, \( \Phi(\mathbf{k}, r_j) \) does not represent the effective scattering factor \( A(\mathbf{k}, r_j) \).

**Sources of Artifacts within the Full-Window Transform**

Using the properties of the CIS inversion, we can examine the behavior of the image function \( U(R) \) from the full-window transform (i.e. Eq. (28)). For those \( \mathbf{k} \) directions within the small window, where the phase of \( \Phi(\mathbf{k}, r_j) \) is quite constant, \( U(R) \) builds up intensity at the jth atom position. However for those \( \mathbf{k} \)'s which are outside the small window, where the phase of \( \Phi(\mathbf{k}, r_j) \) is a strong function of angle, the intensity cannot build up at the jth atom position; instead, it builds up at other places which can produce artifacts. We identify three sources of artifacts that form in the full-window transform; there may be others. The first source is that the paraboloids from different scatterers may overlap in some region of space where they have the same phase. This kind of artifact has a tendency to appear in high-symmetry directions such as rotation axes and mirror planes. The second source of artifacts is the double summation in Eq. (20) when it dominates \( \chi(\mathbf{k}, k) \) in the case \( \left| F(\mathbf{r}_j, k) F^{-1}(\mathbf{k}, k) \right| >> 1 \). When two scatterers line up with the emitter so that \( \mathbf{r}_j// \mathbf{r}_p \), then an artifact will appear at \( R=\mathbf{r}_j-\mathbf{r}_p \). Finally, artifacts may be caused by multiple scattering of the photoelectron. The average intensity from multiple scattering is roughly proportional to \( C^*N^2 \), with \( C \) a coefficient of about a few percent and \( N \) the number of CIS's used in the transform. The intensity at the atomic position \( \mathbf{r}_j \) is roughly proportional to \( n^2 \), with \( n \) the number of CIS's which have same phase for \( \Phi(\mathbf{k}, r_j) \). If all \( \Phi(\mathbf{k}, r_j) \)'s are in phase, the intensity at the position \( \mathbf{r}_j \) would
be proportional to $N^2$, which would make the multiple-scattering intensity negligible. Since the small-window behavior of $\Phi(\mathbf{k}, \mathbf{r})$ makes $n \ll N$, there is the possibility for multiple scattering effects to form considerable intensity (artifacts) comparing to the intensity at the atomic positions.

**Small-Cone Method**

To avoid artifacts and difficulties such as those discussed above, we present the following method for forming the image function:

$$U(\mathbf{R}) = \left| \sum_{\mathbf{k} \in \text{Cone}(-\mathbf{R}, w)} \Phi(\mathbf{k}, \mathbf{R}) \right|^2.$$  \hspace{1cm} (44)

For each point $\mathbf{R}$ in real space, the summation of the CIS inversion is limited to a small set of $\mathbf{k}$ directions which are within a small cone centered in the direction $-\mathbf{R}$ with half-width $w$, instead of the full set of directions as described in Eq. (28). The half-width $w$, usually $15^\circ$-$30^\circ$, is the only adjustable parameter, and can be easily obtained from the experimental $\Phi(\mathbf{k}, \mathbf{r})$ curves like those in Fig. 25.

Figure 26. The choice of the small cone for a given position vector $\mathbf{R}$ in the small cone method. $\theta_e$ and $\varphi_e$ indicates the direction of the axis and $w$ is the half-width of the small cone.
The process is illustrated in Fig. 26. The small-cone method utilizes the most important portion of the diffraction information (see Fig. 25 (b) and (d)). In addition it ensures, within the cone, a uniform scattering phase shift which can be taken to be the value for $\pi$ scattering and can be reliably obtained by theory. This makes it practical to do a phase shift correction for single-element substrates without \textit{a priori} knowledge of the structure, which would not work in the full-window transform[12].

As a procedure for an unknown system, one can first use a small value of $w$, say 10°, to obtain a preliminary image function $U(R)$; then at the positions of the maximum in that function, one uses Eq. (23) to find the experimental curves for the phase and amplitude of the CIS inversion, $\Phi(\hat{k},r)$. From these curves, a value for $w$ is obtained which is used in the final calculation of $U(R)$. Note that while the value of $w$ has little effect on image positions, using larger values of $w$ does improve the image resolution. The effect of the cone-width on the atomic image will be discussed in Appendix B.

At this point, we would like to compare our small-cone method with the small window process used by S. Y. Tong \textit{et al.} [35] to deal with the split images obtained from their simulated spectra. They choose a small angular window in the direction of the split image, and use a window width which comes from the calculated atomic scattering factor $f$. We have used that process, which has some utility but also has two difficulties. First, the position of an atomic image depends on the choice of the direction of the small window, but there is no criterion for choosing the correct direction. Second, the window width is not determined by the atomic-scattering factor $f$ only, but by the effective-scattering factor $A$ which is hard to calculate accurately. In our small-cone
method, the axis of the small cone is chosen automatically as the -\( \hat{R} \) direction [36] and the width is obtained from the experimental data.

**Implementation of Small-Cone Method**

**Inner Potential Correction**

The magnitude and direction of the electron momentum used in the transform must be those inside the sample, \((k, \theta, \varphi)\), which are in principle different from their counterpart outside the sample, \((k(\text{out}), \theta(\text{out}), \varphi(\text{out}))\), due to the different zero-energy levels in the different regions. Inside the sample, the zero-energy level is the top of the so-called muffin tin potential [1], while outside the sample, the zero energy level is the vacuum level. The difference, \(V_0\), is called the inner potential, which is illustrated in Fig. 27(a). The kinetic energy of an electron inside the sample, \(E\), and that outside the sample, \(E(\text{out})\), obey the law of energy conservation:

\[ E = E(\text{out}) + V_0. \]

However, the electron momentum only conserves its component parallel...
to the surface: \( k_{\|} = k_{\|}(\text{out}) \). As a consequence, the electron path is deflected at the surface, as is shown in Fig. 27(b). Considering the relation between \( E \) and \( k \), and \( k_{\|} = k \sin(\theta) \), the electron momentum in the sample can be written in terms of its counterpart outside the sample:

\[
k = \sqrt{k^2(\text{out}) + \frac{2mv_0}{h^2}}.
\]

\[
\theta = \sin^{-1}\left[\frac{k(\text{out}) \sin(\theta(\text{out}))}{k}\right]
\]

\[
\phi = \phi(\text{out}).
\]

Making \( \chi \) continuous

The small-cone method requires that the number of CIS's used and the angular distribution of those CIS's to be the same for all small cones involved. This in turn requires that the normalized diffraction intensity should be a continuous function of the emission angles. In other words, it requires the function \( \chi(k_x, \theta, \phi) \), with the convention that a variable with (without) an integer subscript means a discrete (continuous) variable. However, the normalized diffraction intensity obtained from the experiment and the procedures described in chapter 3 is \( \chi(k_x, \theta, \phi) \), with \( \Delta k(\text{out}) \), \( \Delta\theta(\text{out}) \) constant but \( \Delta\phi \) varying as \( \Delta\theta/\sin(\theta) \). To form a continuous function \( \chi(k_x, \theta, \phi) \) from the discrete data \( \chi(k_x, \theta, \phi) \), a program is developed which uses several subroutines from the IMSL, math library [37] and involves the following procedures. (1) Calculate one-dimensional B-spline coefficients for a continuous function with respect to \( \phi \),
\( \chi(k_{\text{out}}, \theta_{\text{out}}, \phi), \) using the subroutine BSINT. (2) Calculate \( \chi(k_{\text{out}}, \theta_{\text{out}}, \phi), \) with constant \( \Delta \phi \) using the subroutine BSVAL. (3) Calculate two-dimensional B-spline coefficients for a continuous function with respect to variables \( k_{\text{out}} \) and \( \theta_{\text{out}}, \) \( \chi(k_{\text{out}}, \theta_{\text{out}}, \phi), \) using the subroutine BS2IN. (4) Calculate \( \chi(k, \theta, \phi) \) as function of the parameters inside the sample with constant \( \Delta k \) and \( \Delta \theta \), using Eq. (45) and the subroutine BS2VL. (5) Finally, calculate two-dimensional B-spline coefficients for a continuous function with respect to the variables \( \theta \) and \( \phi, \chi(k, \theta, \phi), \) using the subroutine BS2IN again. To calculate the normalized diffraction intensity at point \( (k_i, \theta, \phi) \) in \( k \)-space, simply use subroutine BS2VL and the B-spline coefficients obtained in step (5) above.

**CIS Choice in a Small Cone**

To ensure the same angular distribution of CIS's used with respect to the small-cone axis in all small cones, a set of emission angles \( (\theta_{\text{in}}, \phi_{\text{in}}) \) are chosen in the small-cone coordinate system with the small-cone axis \( (\theta_c, \phi_c) \) chosen as the z direction. Then the angles \( (\theta, \phi) \) from the set \( (\theta_{\text{in}}, \phi_{\text{in}}) \) are calculated in the main coordinate system in which all the experimental data are measured. Refer to Fig. 26. The set \( (\theta_{\text{in}}, \phi_{\text{in}}) \) is chosen by keeping \( \Delta \theta_{\text{in}} \) constant while \( \Delta \phi_{\text{in}} \) is varied as \( \Delta \theta_{\text{in}}/\sin(\theta_{\text{in}}) \) to maintain a constant solid angle for each direction. For each angle, \( (\theta_{\text{in}}, \phi_{\text{in}}) \), the corresponding coordinates in the small-cone coordinate system are:
\[ X_{\text{obj}} = (\sin(\theta_0) \cos(\phi_0), \sin(\theta_0) \sin(\phi_0), \cos(\theta_0)). \]  

For a given position vector \( \mathbf{R} \) with the coordinates \((x_R, y_R, z_R)\), the axis of the small cone is in the direction:

\[ (\theta_c, \varphi_c) = (\cos^{-1}(-z_R), \tan^{-1}(y_R/x_R)). \]  

The matrix of transformation from the small-cone coordinate system to the main coordinate system is:

\[
 M = \begin{pmatrix}
 \cos(\phi_c) & -\sin(\phi_c) & 0 \\
 \sin(\phi_c) & \cos(\phi_c) & 0 \\
 0 & 0 & 1 
\end{pmatrix} \begin{pmatrix}
 \cos(\theta_c) & 0 & \sin(\theta_c) \\
 0 & 1 & 0 \\
 -\sin(\theta_c) & 0 & \cos(\theta_c) 
\end{pmatrix}.
\]  

So the coordinates for \((\theta_0, \varphi_0)\) in the main coordinate system are:

\[ (x_0, y_0, z_0) = X_{\text{obj}} M^*, \]  

where \(M^*\) is the transpose matrix of \(M\). Finally, the angles in the main coordinate system are obtained as:

\[ (\theta_1, \varphi_1) = (\cos^{-1}(z_0), \tan^{-1}(y_0/x_0)). \]  

**Phase Shift Correction**

The last issue is the calculation of the phase shift correction. From the discussion in the second section of this chapter, the effective scattering factor is almost entirely determined by the atomic scattering factor in the small angular window close to the \(\pi\) scattering direction. Also, the phase of the atomic scattering factor is quite constant with
respect to the scattering angle in that region. Thus in the small angular window one can write:

\[ A(k, r) \sim f(\cos(\pi), k) = |f_{\pi}(k)| e^{iA_{\pi}(k)} \]  \hspace{1cm} (51)

Let \[ \Delta(\pi, k) = \Delta_{\pi}(k) + S(\pi) k, \]  \hspace{1cm} (52)

with \( S(\pi) \) the slope of the phase with respect to \( k \) in the direction of \( \pi \) scattering. The effect of this slope in the electron holography calculation is that it shifts the image maximum away from the actual atomic position (see Eq. (24)). To overcome this effect, the necessary phase shift correction in the case of the small-cone method is obtained by modifying the transform Eq. (23) to include the slope \( S(\pi) \):

\[ \Phi(\hat{k}, R) = \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(\hat{k}, k) e^{-i(\hat{k} \cdot R(1 - \hat{k} \hat{R}) + S(\pi))} \hat{g}(k) dk. \]  \hspace{1cm} (53)
CHAPTER V

RESULTS FROM SMALL-CONE METHOD

Four sets of experimental data were analyzed with the small-cone method. They are Si(111)√3x√3-Al, Si(111)√3x√3-Ga, Si(111)1x1-As and Si(100)1x2-As. The diffraction data used in the analysis were all taken from the adatom core-level photoemission. The procedures for preparing the clean Si surface, the surface quality monitoring, the typical EDC resolution, and the momentum step Δk were described in the last section in Chapter 3. For the Si(111)√3x√3-Al system, the same analysis conditions are used as in the case of the full-window transform. For all other systems, a 10 ev inner potential V₀ (a typical value used in the LEED I-V method) and a -0.18 Å phase slope, s(π), calculated for Si in the π scattering direction are used in the small-cone method. The effect of including the inner potential is to move apparent atomic positions deeper for those atoms far away from the normal direction and to shorten the bond length. The effect of the -0.18 Å phase slope is to increase the bond length by about 0.1 Å.
Si(111)$\sqrt{3}\times\sqrt{3}$-Al

Using the procedures described in Chapter 3, the angular dependence of the phase and amplitude of the CIS inversion at the positions of Si atoms A and D were obtained, and are shown in Fig. 28. For atom A, the emitter-scatterer direction is at about 60° polar angle, while for atom D, it is about 0° polar angle. The results show the "small window" behavior clearly with a half-width $w$ about 25°. Using this half-width value, the resultant image functions are shown in Fig. 29. Panel (a) is the X-Z planar cut, with the Al represented by a cross at the origin. This result clearly shows the Si atoms A and D with much improved signal-to-background ratio compared to the same cut from the full-window transform, Fig. 22(a). Panels (b) and (c) of Fig. (29) are the horizontal planar cuts passing through the first- and second-layer Si atoms, respectively. The pronounced artifacts shown in Fig. 22(b) from the full-window transform do not appear in the same cut, panel (b) of Fig. (29). Panel (d) is the three-dimensional constant-intensity surface plot. The Al atom is represented by the sphere O. The Si atoms A, B and C are indicated at 50% of their maximum intensity, while the Si atom D is indicated at 60% of its maximum intensity. Referring to the Si(111) clean surface structure shown in Fig. 23, we conclude that the Al atoms occupy the $T_4$ site. The three curves in panel (e) of Fig. (29) show the line scans passing through the Si atom D in three directions, which indicate the atomic position and the typical space resolution. The atomic positions obtained from the small-cone method are compared in Table 2 with those obtained from the LEED I-V
Figure 28. Phase (a) and amplitude (b) of the CIS inversion at the position of Si atom A as a function of polar angle for Si(111)\sqrt{3}\times\sqrt{3}-Al. The azimuthal angle is 0°.
Figure 28. Phase (c) and amplitude (d) of the CIS inversion at the position of Si atom D as a function of polar angle for Si(111)$\sqrt{3}\times\sqrt{3}$-Al. The azimuthal angles are $0^\circ$ and $180^\circ$ for the positive and negative polar angle values, respectively.
Figure 29 (a) Vertical planar cut of the image function as obtained from the small-cone method for Si(111)$\sqrt{3}\times\sqrt{3}$-Al. The cross represents the Al atom. Peaks marked A and D are due to Si atoms. Coordinate Unit: Å.
Figure 29 (b) X-Y planar cut passing through the first-layer Si atoms at z=-1.2 Å of the image function as obtained from the small-cone method for Si(111)$\sqrt{3}x\sqrt{3}$-Al. Coordinate Unit: Å.
Figure 29 (c) X-Y planar cut passing through the second-layer Si atoms at \( z = -2.5 \, \text{Å} \) as obtained from the small-cone method for \( \text{Si}(111)\sqrt{3} \times \sqrt{3}-\text{Al} \). Coordinate Unit: Å.
Figure 29(d) Three-dimensional constant-intensity surface plot of the image function for Si(111)√3x√3-Al. The Al atom is represented by the sphere O since it is the emitter. Atoms A, B and C are plotted at 50% of their maximum intensity, while atom D is plotted at 60% of its maximum intensity.
Figure 29 (e) Line scans of the image function obtained from the small-cone method for Si(111)\sqrt{3}x\sqrt{3}-Al. Coordinate Unit: Å.
method [33] and from first-principles pseudopotential total-energy and force calculations [38]. The maximum discrepancy among these positions is about 0.1 Å.

Table 2. Comparison of atomic positions for Si(111)√3x√3-Al obtained from this method, from the LEED I-V method and from theoretical calculations (Coordinate Unit: Å)

<table>
<thead>
<tr>
<th></th>
<th>(A_x)</th>
<th>(A_y)</th>
<th>OA</th>
<th>OD</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Work</td>
<td>-2.2</td>
<td>-1.2</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>LEED I-V</td>
<td>-2.1</td>
<td>-1.2</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Calculation</td>
<td>-2.1</td>
<td>-1.3</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

\(\text{Si}(111)\sqrt{3}\times\sqrt{3}\text{-Ga}\)

The Ga flux was obtained by evaporation from a tantalum basket. About 2 ML Ga was deposited on the clean Si(111) 7x7 surface, and the sample was annealed at about 700 °C for 2 minutes to obtain a sharp \(\sqrt{3}\times\sqrt{3}\) structure as shown in Fig. 19(a). The reference direction for \(\varphi=0°\) is the same as for Si(111)\(\sqrt{3}\times\sqrt{3}\)-Al, which is also shown in Fig.19(a). Figure 30(a) shows a typical wide-scan energy distribution curve for this system, at 150 ev photon energy. A total of 74 CIS's were taken from the Ga 3d core level emission. The angular range is 0~82.5° in polar angle with \(\Delta\theta=7.5°\) and 0~60° in azimuthal angle. The momentum range is about 4.6~7.6 (1/Å). Fig. 30(b) shows some typical CIS curves together with the computer-chosen non-diffractive curve \(I_0(k)\).

Using a 20° half-width as dictated by the data in Fig. 25, the resultant images \(U(R)\) are shown in Fig. 31. Panel (a) is the X-Z planar cut with Ga emitter position at the
Figure 30. (a) Wide-scan Energy Distribution Curve (EDC) for Si(111)$\sqrt{3} \times \sqrt{3}$-Ga. $h\nu = 150$ ev.
Figure 30. (b) Representative experimental curves of $I(k)$ (CIS) (circles and solid lines) from the Ga 3d with computer-chosen $I_0(k)$ (dashed lines) for Si(111)$\sqrt{3}$x$\sqrt{3}$-Ga. The short bars on the left side are the baselines for the corresponding curves.
Figure 31 (a) Vertical planar cut of the image function as obtained by the small-cone method for Si(111) $\sqrt{3}\times\sqrt{3}$-Ga. The cross represents the Ga atom. Intensity maxima marked A, D and E are due to Si atoms. Coordinate Unit: Å.
Figure 31 (b) X-Y planar cut passing through the first-layer Si atoms at \( z = -1.5 \) Å of the image function as obtained from the small-cone method for Si(111)\( \sqrt{3} \times \sqrt{3} \)-Ga. Coordinate Unit: Å.
Figure 31 (c) X-Y planar cut passing through the second-layer Si atoms at $z=-2.4$ Å of the image function as obtained from the small-cone method for Si(111)$\sqrt{3}x\sqrt{3}$-Ga. Coordinate Unit: Å.
Figure 31 (d) X-Y planar cut passing through the third-layer Si atoms at $z = -4.8$ Å of the image function as obtained from the small-cone method for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga. Coordinate Unit: Å.
Figure 31(e) Three-dimensional constant-intensity surface plot of the image function for Si(111) \( \sqrt{3} \times \sqrt{3} \)-Ga. The Ga atom is represented by the sphere O since it is the emitter. Si atoms A, B, C, and D are plotted at 60% of their maximum intensity, while atom E is at 70% of its maximum intensity.
origin (the cross). It shows atoms A, D and E clearly. Shown in panels (b), (c) and (d) are the horizontal planar cuts passing through the first-, second- and third-layer Si atoms respectively. Comparing the results with those in Fig. 24 (a) and (b) from the full-window transform, one sees a much improved image from the small-cone method. Panel (e) shows the three-dimensional constant-intensity surface plot of the image function. The Ga is represented by the sphere O. The Si atoms A, B, C and E are represented by the 60% contour of their maximum intensity, while the Si atom E is represented by its contour at 70%. Comparing the structure in panel (e) with the structure of the clean Si(111) surface shown in Fig. 23, it is clear that Ga binds to Si atoms A, B and C, occupying the so-called T4 site. The same result was obtained earlier by the LEED I-V method using much more effort and by using model calculations. The atomic positions obtained from the small-cone method are compared in Table 3 with those from the LEED I-V method [39]. The maximum discrepancy is about 0.2 Å.

Table 3. Comparison of atomic positions for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga obtained from this method, and from the LEED I-V method (Coordinate Unit: Å).

<table>
<thead>
<tr>
<th></th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>OA</th>
<th>OD</th>
<th>OE</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Work</td>
<td>-1.9</td>
<td>-1.5</td>
<td>2.4</td>
<td>2.4</td>
<td>4.8</td>
</tr>
<tr>
<td>LEED I-V</td>
<td>-2.10</td>
<td>-1.35</td>
<td>2.50</td>
<td>2.57</td>
<td>4.71</td>
</tr>
</tbody>
</table>
After the sharp 7x7 LEED pattern was obtained in the analysis chamber, the Si(111) sample was transferred to the middle chamber ((2) in Fig. 11). The arsenic flux was evaporated from a tungsten basket in the middle chamber. During the As deposition, the As pressure was about 5x10^-7 torr as measured by a gauge far away from the source; the estimated As pressure on the sample was in the 10^-5 torr range. The sample was kept at 350 °C and the As deposition lasted 3 minutes. When the sample was transferred back to the analysis chamber, it showed a good 1x1 LEED pattern, which was further improved by annealing for three minutes at 400 °C. The 1x1 LEED pattern is composed of only the dots (without the crosses) shown in Fig. 19(a) and the reference direction for φ=0° is the same as for Si(111)v3xv3-Al and Si(111)v3xv3-Ga. Figure 32(a) shows a typical wide-scan energy distribution curve for this system at 150 ev photon energy. A total of 95 CIS's were taken from the As 3d core level emission. The angular range is 0–82.5° in polar angle with Δθ=6.0° and 0–60° in azimuthal angle. The momentum range is about 3.8–7.2 (1/Å). Figure 32(b) shows some typical CIS curves together with the computer-chosen non-diffractive curve I₀(k).

The angular dependence of the phase and amplitude of the CIS inversion at the position of Si atom D is shown in Fig. 33. For this atom, the emitter-scatterer direction is at about 70° polar angle. The small-window behavior in Fig. 33 gives a half-window width of about 30° which is used in the transform. The resultant images are shown in Fig.
Figure 32. (a) Wide-scan Energy Distribution Curve (EDC) for Si(111)1×1-As
Figure 32. (b) Representative experimental curves $I(k)$ (CIS) (circles and solid lines) from the As 3d with computer-chosen $I_0(k)$ (dashed lines) for Si(111)1x1-As. The short bars on the left side are the baselines for the corresponding curves.
Figure 33. Phase (a) and amplitude (b) of the CIS inversion at the position of Si atom D as a function of polar angle for Si(111)1x1-As. The azimuthal angle is 180°.
Figure 34 (a) Vertical planar cut of the image function as obtained from the small-cone method for Si(111) 1x1-As. The cross represents the As atom. The peak marked D is due to a Si atom. Coordinate Unit: Å.
Figure 34 (b) X-Y planar cut passing through the first-layer Si atoms at \( z = -1.0 \text{ Å} \) of the image function as obtained from the small cone method for Si(111)1x1-As. Coordinate Unit: Å.
Figure 34(c) Three-dimensional constant-intensity surface plot of the image function for Si(111)1x1-As. The As atom is represented by the sphere A since it is the emitter. The Si atoms A, B and C are plotted at 60% of their maximum intensity.
34. Panel (a) is the X-Z planar cut with the As emitter on the origin (the cross). It shows only one atom on the side and no atoms below the As atom. The signal-to-noise ratio is much improved over the result from the full-window transform (see Fig. 24(c)). Panel (b) is the horizontal planar cut passing through atom D. Panel (c) shows the three-dimensional constant-intensity surface plot of the image function. The As is represented by the sphere O. The Si atoms A, B, C are indicated at the 60% of their maximum intensity. By comparing the structure in panel (c) with the structure of the clean Si(111) surface shown in Fig. 23, and considering the 1x1 LEED pattern, we conclude that the only possible site for As is that in which the As atom replaces the top silicon atoms such as atom A and binds to Si atoms D, E and F. This result agrees with the results of Uhrberg et al obtained from energy-band fitting [40]. The Z coordinate for the Si atom D obtained from this method is -1.0 Å, which agrees well with the calculated value -0.97 Å [40] and the result obtained from the x-ray standing wave measurement, -0.95 Å [41]. The X coordinate of atom D is 2.3 Å from this method, which is very close to the dimension for an ideal Si crystal, 2.2 Å, consistent with the observation that the LEED pattern is 1x1.

Si(100)1x2-As

This is the first system in holography study with emitters occupying two non-equivalent sites (the two sites have different environment), so it is much more complicated.
The clean Si(100) surface has a 2x1 reconstruction due to the dimerization of the top-layer Si atoms. A typical (100) surface is composed of many terraces separated by single-layer steps. As a consequence, adjacent terraces have dimer directions perpendicular to each other forming a mixed LEED pattern: 2x1+1x2. It is found that a vicinal (100) surface with the normal direction about 4° off the (100) has only double-layer steps with terrace width about 40 Å [42]. Therefore the dimer directions are all the same on the entire surface forming a single-domain 2x1 LEED pattern. This is shown schematically in Fig. 35(a). To make the system simpler, this vicinal Si(100) surface is chosen in this work. Using the same conditions as in the case of Si(111), an excellent single-domain 2x1 LEED pattern which is purely rectangular was obtained.

Depending on the conditions, the deposition of As on the single-domain Si(100)2x1 substrate can result in two different structures: perpendicular As dimers (1x2 LEED pattern) and parallel As dimers (2x1 LEED pattern). In this work, the former type was chosen and the conditions used by Bringans et al [43] were followed. After the single-domain Si(100) 2x1 sample was transferred to the middle chamber, the As source was heated up to 210 °C as measured by a thermocouple fixed on the tungsten basket, producing an As pressure in the range of 10⁻⁵ torr. Then the sample was heated gradually to 700 °C in 2 minutes, and kept at that temperature for 3 minutes, after which the sample current was gradually turned down to 0 in 2 minutes. After the sample was cooled down to room temperature in another 4 minutes, the As source power was turned off. When the sample was transferred back to the analysis chamber, it showed a 1x2 LEED pattern, the perpendicular As dimer pattern which is 90° rotated from the clean Si dimer
Figure 35 (a) Clean Si(100) 4° 2x1 single domain composed of Si dimers parallel to the edge direction. The step height is two-atomic layers. The terrace length L is about 40 Å.
Figure 35 (b) Representative experimental curves of I(k) (CIS) (circles and solid lines) from the As 3d with computer-chosen I₀(k) (dashed lines) for Si(100)1x2-As. The short bars on the left side are the baselines for the corresponding curves.
Figure 36. Phase (a) and amplitude (b) of the CIS inversion at the position of Si atom A as a function of polar angle for Si(100)1x2-As. The azimuthal angle is 15°.
2x1 pattern. The reference direction for $\varphi=0^\circ$ is chosen along the step edge direction.

A total of 95 CIS's were taken from the As 3d core level emission. The angular range is $0\sim82.5^\circ$ in polar angle with $\Delta \theta=7.5^\circ$ and $0\sim90^\circ$ in azimuthal angle. The momentum range is about $4.2\sim7.2$ (1/Å). Fig. 35(b) shows some typical CIS curves together with the computer-chosen non-diffractive curve $I_0(k)$.

The angular dependence of the phase and amplitude of the CIS inversion at the position of Si atom A is shown in Fig. 36. For this atom, the emitter-scatterer direction is at about $60^\circ$ polar angle. The small-window behavior in Fig. 36 gives a half-window width of about $30^\circ$ which is used in the transform. The resultant images are shown in Fig. 37. Panel (a) is the horizontal planar cut passing through the As atom layer. There are four spots of high intensity. However as will be discussed later, the two spots on the x-axis are not associated with real atoms. The other two spots correspond to the two different As emitters P and Q which form the As dimer. The symbol Q/P labels structure that uses the electron emission from atom P to probe the surroundings including atom Q. For this reason, the separation between the Q/P and P/Q spots is twice the As-dimer bond length. Panel (b) is a horizontal planar cut passing through the first-layer Si atoms, which shows four Si atoms at $x=-1.8$ Å and $x=1.8$ Å respectively. The symbols use the same convention as in panel (a). Thus the separation between A/P and D/P along the x-axis is the actual separation between Si atoms A and D, since the two peaks are viewed from the same emitter P. However the separation between A/P and B/Q is not the actual separation between Si atoms A and B, since these two peaks are viewed from the two different As
Figure 37(a) X-Y Planar cut for the top-layer of the image function as obtained from the small-cone method for Si(100)1x2-As. The origin is the overlap of As atoms P and Q. Q/P labels the image of As atom Q formed from the As emitter P. Coordinate Unit: Å.
Figure 37 (b) X-Y planar cut passing through the first-layer Si atoms at \(z=-1.5\ \text{Å}\) of the image function as obtained from the small-cone method for Si(100)1x2-As. Coordinate Unit: Å.
Figure 37 (c) Y-Z planar cut of the image function at x= -1.8 Å as obtained from the small-cone method for Si(100) 1x2-As. The cross represents the As atom P and Q (together). The intensity maxima marked A/P and B/Q are due to Si atoms. Coordinate Unit: Å.
Figure 37(d) Three-dimensional constant-intensity surface plot of the image function for Si(100) 1x2-As. The As atoms P and Q are represented by spheres. Si atoms A, B, C and D are plotted at 70% of their maximum intensity.
emitters P and Q, respectively. Instead it is the difference between the separation of Si atoms A and B and the separation of the emitters P and Q. Panel (c) is a Y-Z planar cut with x=-1.8 Å which gives the depth of the first-layer Si atoms. Panel (d) shows the three-dimensional constant-intensity plot of the image. The two different As emitters are represented with the spheres P and Q. The Si atoms A, B, C and D are indicated at 70% of their maximum intensity.

We now return to panel (a) in Fig. 37. The two spots on the x-axis are formed from the overlap of the paraboloids passing through the first-layer Si atoms. Figure 38(a) shows the effective system when the two nonequivalent emitters P and Q are put together at the origin for the real system Si(100)1x2-As. The symbols on the spheres follow the convention discussed above. The small angular window in the Figure points from the emitter to the atom D/P. There are five sticks in the small window: four on the edge and one on the center. They represent five typical emission directions. Imagine putting five more such small angular windows which point from the emitter to the atoms A/P, B/Q, C/Q, P/Q and Q/P, respectively. In total there are 30 emission directions with 5 directions in each small window. The CIS taken in each direction gives a paraboloid passing through the atom at that direction. The projection on the As plane of the 30 paraboloids is shown in Fig. 38(b). The two intersections on the y-axis correspond to the two As emitters P and Q. There are even more paraboloids that pass the x-axis in the region of -3-2 Å and 2-3 Å, which could form a huge intensity and generate the two spots on the x-axis shown in Fig. 37(a).
For this system, Northrup et al. [44] calculated the structure, Zegenhagen et al. [45] measured the vertical distance between the As layer and the first Si layer using the x-ray standing wave method, and Jedrecy et al. [46] measured the As dimer length using grazing incidence x-ray diffraction technique. The comparison of the atomic positions is given in Table 4. The maximum discrepancy is about 0.2 Å.

Table 4. Comparison of atomic positions for Si(100)1x2-As obtained from this method, XSW, GIXD and theoretical calculation (Coordinate Unit: Å).

<table>
<thead>
<tr>
<th></th>
<th>( A_x )</th>
<th>( A_y )</th>
<th>( A_z )</th>
<th>( PA )</th>
<th>( PQ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>This method</td>
<td>-1.8</td>
<td>-0.5</td>
<td>-1.5</td>
<td>2.4</td>
<td>2.3</td>
</tr>
<tr>
<td>*XSW, **GIXD</td>
<td></td>
<td></td>
<td>*-1.26</td>
<td></td>
<td>**2.55</td>
</tr>
<tr>
<td>Calculation</td>
<td>-1.92</td>
<td>-0.52</td>
<td>-1.41</td>
<td>2.44</td>
<td>2.55</td>
</tr>
</tbody>
</table>
Figure 38 (a) The effective system when the two different As emitters are put together at the origin for the real system Si(100)1x2-As. The symbol P/Q labels the image of atom P formed from the emitter Q. The small window points from the emitter to the Si atom D/P. There are five sticks in the small window: four on the edge and one on the center. They represent five typical emission directions.
Figure 38 (b) The projection on the As plane of 30 paraboloids which are from six small windows pointing from the emitter to the "atoms" A/P, B/Q, C/Q, D/P, P/Q and Q/P shown in Fig. 38(a). There are five emission directions in each small window. For each CIS taken in one direction in a small window, there is one paraboloid passing through the atom on the axis of that window.
CHAPTER VI

DISCUSSION AND CONCLUSIONS

Comparison of Related Methods

Encouraged by the wealth of structural information available in low-energy photoelectron diffraction, several different methods have been devised to analyze the diffraction data. In addition to the methods discussed before, namely EXAFS, SEXSFS (one dimensional information), single-energy holography, and full-window transform, there is one more method, the pathlength method of Schindler et al [47,48] which uses almost the same kind and same amount of experimental data as our small-cone method does. The method uses the phenomenon that the diffraction amplitude has a local maximum in the π scattering direction (refer to Fig. 25, 28, 33 and 36) to locate the scatterer's direction, and uses one-dimensional Fourier transform to obtain the bond length. Essentially, the method is the zero-width limit (w=0°) of our small-cone method, and therefore it does not make good use of the diffraction information. For comparison, we analyze our Si(111)√3x√3-Ga and Si(111)√3x√3-Al data using the pathlength method.
Figure 39(a) Contour plot of the image function as obtained from the pathlength method of Schindler et al for Si(111) $\sqrt{3} \times \sqrt{3}$-Ga. The plane is at $\phi=0^\circ$. 
Figure 39(b) Contour plot of the image function as obtained from the pathlength method of Schindler et al for Si(111) √3x√3-Al. The plane is at φ=0°.
and display the results using the format of Schindler et al. Figure 39 (a) shows the image intensity as a function of the pathlength difference and the polar angle at the azimuthal angle $\phi=0^\circ$ for Si(111)\textsqrt{3}x\textsqrt{3}-Ga. The maximum intensity for the Si atom D does not appear at $0^\circ$ polar angle as shown in Fig. 31(a); instead it is shifted by $7^\circ$. Figure 39(b) is the same kind of contour plot for Si(111)\textsqrt{3}x\textsqrt{3}-Al. The maximum intensity is shifted away from the correct direction $0^\circ$ (see Fig. 29(a)) by $10^\circ$. This directional shift inherent in Schindler's method is caused by the neglect of the large-angle scattering contribution from other atoms, in the present case from the Si atoms A, B and C. This problem is reported to be generally present by A. P. Kaduwela et al.[49].

Let us now compare the related methods. Figure 40 schematically shows the main characteristic of each method, where the radial direction in the upper half of the plot represents the momentum magnitude. From the discussions in Chapters 4 and 5, for the scatterer located at the position $r$, most of the diffraction information is confined in the small angular window centered at the direction $-r$ and with a half-width of $w$. The single-energy holography (SEH) method uses the information on the half circle with momentum $k_2$. However the effective information about the scatterer is only on the short arc AB. The momentum change parallel to the radial direction, $\Delta k_{\parallel}$, is small over this arc. This leads to considerable uncertainty for the scatterer position determination in the radial direction, $\Delta R_{\parallel}$, since the relation $\Delta k_{\parallel} \Delta R_{\parallel}$ ~ constant is generally true for the Fourier transform. Also the information on the other part of the half circle could degrade the image by forming artifacts. The full-window transform uses the information in the sector
Figure 40. Schematic comparison of related methods. The radial direction on the upper half of the plot represents the momentum magnitude.
confined by the two half circles at the radial distance $k_1$ and $k_2$. The effective momentum change in the radial direction is about $k_2-k_1$, which is much larger than that in the case of SEH. Therefore the space resolution in this direction is much improved. However the information outside the small window could generate significant artifacts as discussed before. The pathlength method of Schindler et al essentially uses only the information in one direction, $-\mathbf{r}$ direction. The insufficient information leads to the directional shift of the image discussed above. Our small-cone method uses the right part and the right amount of the available information, the area ABCD, which is the physical reason for the success of this method.

Conclusions

1. This is the first work that successfully implemented the full-window transform of S. Y. Tong et al to directly determine the adsorbate position using energy-dependent and angle-resolved photoelectron diffraction. The result for Si(111)\sqrt{3}\times\sqrt{3}-Al clearly shows the Si atoms around the emitter Al and identifies the Al as occupying the T$_4$ site. This is the best atomic image ever published, with no twin image and with good atomic position values.

2. This is also the first work that found and finally solved the problem with the full-window transform: significant artifacts in the atomic image. To understand and solve the
problem, for the first time, a crucial function - the effective scattering factor - is extracted from the experimental data. The result shows that a small angular window exists close to the emitter-scatter direction. Inside this window, the effective scattering factor has a fairly constant phase and relatively larger amplitude. Outside this window, the effective scattering factor has rapidly changing phase and smaller amplitude. This "small window" behavior is proved general by our theoretical analysis and is suggested to be responsible for the artifacts from the full window transform. As a consequence, we proposed a new transform scheme - the small-cone method. To calculate the image function intensity at a given position vector in real space, we now use only those diffraction curves with their emission directions within a small cone, the axis of which is opposite to the given position vector. The width of the small cone can be readily obtained from the experimental data. The use of this small-cone method dramatically reduces the artifacts for all the data sets obtained.

3. This work has obtained interesting results for several additional systems.

For Si(111)\(\sqrt{3}\times\sqrt{3}\)-Ga, the image reveals that the Ga atoms also occupy the T\(_4\) site. The image for the Si(111)1x1 - As structure shows that the As atoms substitute for the top-layer Si atoms. The result for the more complicated structure Si(100)1x2 - As clearly shows the adatom dimer. This image is the first obtained for a two-site structure. The atomic position values obtained from this small-cone method are very close to those obtained from theoretical calculations and from other experimental methods, i.e., the
LEED method, the x-ray standing wave method, and the grazing incidence x-ray diffraction method. The maximum discrepancy is about 0.2 Å.

4. This small-cone method can be used for any ordered adsorbate systems with one or two nonequivalent emitters. The best initial states are 1s, 2p, 3d and 4f, which produce larger and smoother photoexcitation cross sections. The best kinetic energy range of the photoelectron is about 70–400 ev, which guarantees enough diffraction oscillations to obtain high space resolution. If a position-sensitive detector is available, the data from the entire emission hemisphere will help to further reduce noise and will be able to distinguish symmetric and asymmetric dimers. If more accurate atomic positions are desired, one can further use a trial-and-error method to refine the results from the small-cone method.

I believe that the small-cone method will play an important role in future interface studies.
APPENDIX A

ADJUSTMENT OF THE HEMISPHERICAL ANALYZER
APPENDIX A

ADJUSTMENT OF THE HEMISPHERICAL ANALYZER

In case of an adjustment of the hemispherical analyzer (HA50) is necessary, the following method is used.

A point object is attached to a three-dimensional adjustable micrometer which is fixed to a stationary base. Then the point of the object is positioned at the rotation center of the goniometer as close as possible and is illuminated by a He-Ne laser from the Y direction so that it can be observed clearly. The analyzer is rotated to the positive X direction in the horizontal plane (the X-Y plane), which is shown in upper panel of Fig. 41. Look through the small hole on the analyzer from A to B, and move the point object along the Y direction to the view center. If the axis of the analyzer is off from the radial direction by an angle $\alpha$ in this plane, the point object will be moved to the point C. Then the analyzer is rotated 180° to the -X direction and the above procedure is repeated. Now, the point object will be moved to the point D. The angle $\alpha$ can be calculated to be $\alpha = (\text{Distance between C and D}) / L$, with L the diameter of the rotation circle for the back-hole of the analyzer.

Next, move the point object to the edge of the rotation circle of the analyzer, keeping it in the horizontal plane. Look through the small hole from A to B and adjust the
Figure 41. Adjustment of the hemispherical analyzer. The upper panel shows the way measuring the angle by which the axis of the analyzer is off from the radial direction in the horizontal plane. The lower panel shows the measurement of the off angle in the vertical plane.
point of the object to the view center along the Z direction, as is shown in the lower panel of Fig. 41. If the axis of the analyzer is off from the radial direction by an angle $\beta$ in the vertical plane (the X-Z plane), the point object will be moved to the point F. Now, move the point object to the left edge of the rotation circle and look through the small hole from B to A. The point of the object will be moved to the point E. The angle $\beta$ is calculated simply as: $\beta = \frac{\text{Vertical Distance between E and F}}{L}$.

To adjust the analyzer parallel to the radial direction in both the horizontal and vertical planes, put Al foil with right thickness on the right edge between the analyzer head and the analyzer support to compensate the measured angles $\alpha$ and $\beta$. The value of $L$ is about 200 mm. If the accuracy for the distance measurement is 0.5 mm, an accuracy of about 0.2° for the determination of the angles $\alpha$ and $\beta$ can be obtained.
APPENDIX B

EFFECT OF THE SMALL-CONE WIDTH
APPENDIX B

EFFECT OF THE SMALL-CONE WIDTH

The effect of the small-cone width on the atomic image is shown in Fig. 42 with the x-z planar cuts for Si(111)√3x√3-Ga. The images are obtained with no inner potential correction or phase shift correction. When the small-cone width is reduced gradually from panel (a) to panel (f), the artifacts are reduced correspondingly. The larger artifacts shown in the full-window panel (180°) begin to disappear between 20°-30°, which agrees with the small-window width shown in Fig. 25. The atomic positions obtained with the cone-width between 10° and 30° are almost the same, but the space resolution becomes better when the cone-width increased in this region. When the width goes to 0°, the spot below the Ga atom is shifted from the z-axis, a phenomenon discussed in the first section of Chapter 6 for Schindler's pathlength method[47,48]. The best image is obtained with the cone-width of 20°, which corresponds to the width shown in Fig. 25.
Figure 42 (a) Vertical planar cut of the image function for Si(111)\sqrt{3}\times\sqrt{3}\text{-Ga} with a cone-width of 180°. The cross represents the Ga atom. Coordinate Unit: Å.
Figure 42 (b) Vertical planar cut of the image function for Si(111)√3x√3-Ga with a cone-width of 90°. The cross represents the Ga atom. Coordinate Unit: Å.
Figure 42 (c) Vertical planar cut of the image function for Si(111)√3x√3-Ga with a cone-width of 40°. The cross represents the Ga atom. Coordinate Unit: Å.
Figure 42 (d) Vertical planar cut of the image function for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga with a cone-width of 30°. The cross represents the Ga atom. Coordinate Unit: Å.
Figure 42 (e) Vertical planar cut of the image function for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga with a cone-width of 20°. The cross represents the Ga atom. Coordinate Unit: Å.
Figure 42 (f) Vertical planar cut of the image function for Si(111)$\sqrt{3} \times \sqrt{3}$-Ga with a cone-width of $10^\circ$. The cross represents the Ga atom. Coordinate Unit: Å.
Figure 42 (g) Vertical planar cut of the image function for Si(111)$\sqrt{3}\times\sqrt{3}$-Ga with a cone-width of 0°. The cross represents the Ga atom. Coordinate Unit: Å.
REFERENCES
REFERENCES


23. From the documents in the Winsconsin Synchrotron Radiation Center.


26. Fitted from the resolution curves in the documents in the Winconsin Synchrotron Radiation Center.


31. Software MATHEMATICA, Wolfram Reserch Inc. 100 Trade Center Drive, Champaign, IL 61820.


36. Independently, Hua Li and S. Y. Tong et al. presented same small window idea at March APS meeting (1994).


