LEED STUDIES ON TWO SURFACES OF COPPER

by

SEAN RICHARD PARKIN
B.Sc., The University of Kent at Canterbury 1987

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
JUNE 1989
© Sean Richard Parkin
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver, Canada

Date 25th July 1989
Abstract

The work presented in this thesis includes investigations using low energy electron diffraction (LEED) of the clean stepped Cu(311) surface and its interactions with sulphur, and also for a half monolayer oxygen superstructure on Cu(110) designated Cu(110)-(2x1)-O. In each case, intensity versus energy (I(E)) curves were measured with a video LEED analyzer for sets of independent diffracted beams for future comparison to the results of multiple scattering calculations.

The clean Cu(311) surface was cut and polished from a single crystal copper rod and cleaned by sputter-etching with argon ions followed by annealing. Intensity measurements were recorded for 14 symmetry inequivalent diffraction beams at normal incidence, followed by six at 10° off normal incidence. Adsorption of sulphur on the Cu(311) surface was carried out by dosing with H₂S followed by its presumed dissociation and loss of hydrogen to the vacuum. This study indicated that S atoms order themselves on Cu(311) only in the [01\bar{1}] direction. In addition to experimental work on the Cu(311) surface, a discussion is made of the difficulties associated with the application of LEED to adsorption on stepped surfaces.

The Cu(110)-(2x1)-O structure was prepared by the adsorption of oxygen on the (110) surface of copper. The conditions necessary to produce the best LEED pattern were found by analysis of adsorption spot profiles, and experimental LEED I(E) curves were recorded for nine independent beams at normal incidence and a further six at 10° off normal incidence.
# Table of contents

Abstract ii  
Table of Contents iii  
List of Tables v  
List of Figures vi  
Acknowledgements xi  

Chapter 1 An Introduction to Low Energy Electron Diffraction 1  
1.1 Modern Surface Science 2  
1.2 Classification of Surface Structures 4  
1.2.1 The Step and Microfacet Notations for Stepped Surfaces 4  
1.2.2 The Unit Mesh and Reciprocal Net 7  
1.2.3 Overlayer Structures - Wood and Matrix Notations 9  
1.3 Low Energy Electron Diffraction 10  
1.3.1 Electron Scattering 10  
1.3.2 Conditions for Elastic LEED 14  
1.3.3 Surface Crystallography by LEED 18  
1.3.4 Calculation of LEED Intensities 21  
1.3.5 Evaluation of LEED I(E) Curves 25  
1.4 Auger Electron Spectroscopy 27  

Chapter 2 Experimental Methods 31  
2.1 Vacuum Chamber and Pumpdown 32  
2.2 Sample Preparation and Cleaning 35  
2.3 AES for Surface Composition Analysis 37
2.4 Experimental LEED
   2.4.1 LEED Optics and Electron Gun  39
   2.4.2 LEED Spot Intensity Measurements  41
   2.4.3 LEED Spot Profile Measurements  43

Chapter 3 Studies on the Copper (311) Surface  47
   3.1 Introduction  48
   3.2 Experimental Work on the Clean Copper (311) Surface  50
   3.3 Adsorption of Sulphur on Cu(311)  53
      3.3.1 Introduction  53
      3.3.2 Experimental  63
      3.3.3 Interpretation of the LEED Pattern for Sulphur on Cu(311)  65
   3.4 Some Considerations for Adsorption on Stepped Surfaces  70

Chapter 4 Studies of the Copper (110)-(2x1)-O Adsorption system  77
   4.1 Introduction and Previous Work  78
   4.2 Experimental  83
   4.3 Presentation of Data  85
   4.4 Final Comments and Suggestions for Further Work  94

References  96
List of tables

1.1 Some surface sensitive techniques. 3
1.2 Examples of the step and microfacet notations for some f.c.c. stepped surfaces 6
3.1 Current crystallographic data for the (311) surfaces of some f.c.c. metals. 51
3.2 Beam indices and energy ranges (eV) for the experimental Cu(311) LEED I(E) curves. 54
3.3 Characteristics of the seven simplest f.c.c. stepped surfaces. 73
3.4a Some characteristics of the three simplest b.c.c. high Miller index surfaces with rectangular unit meshes. 74
3.4b Some characteristics of the four simplest non-basal h.c.p. surfaces with rectangular unit meshes. 75
4.1 Current structural information for the Cu(110)-(2x1)-O adsorption system. 80
4.2 Beam indices and energy ranges (eV) for the experimental Cu(110)-(2x1)-O LEED I(E) curves. 86
List of figures

1.1 The five Bravais two dimensional meshes in real and reciprocal spaces. 8
1.2 Wood and matrix notations for some overlayer structures on the f.c.c.(110) surface. 11
1.3 A typical energy distribution of backscattered electrons as a function of the primary beam energy $E_p$. 13
1.4 Typical energy distribution of electron mean free paths, $L$, in a metallic solid. 13
1.5 The geometry of the LEED experiment; an electron beam is incident on a surface with energy $E$ in a direction $(\theta, \phi)$. The intensity of the diffracted beam is recorded as a function of $E$. 15
1.6 The Ewald sphere construction for LEED. The Ewald sphere is shown at two energies for the same incident direction (view parallel to the surface). 19
1.7 Five types of adatom structure on the f.c.c.(110) surface. Each would produce a (2x1) LEED pattern, illustrating that structural analyses require more than just knowledge of the diffraction pattern. 20
1.8 Three types of domain structure found for overlayers on f.c.c. crystal faces. 22
1.9 Schematic diagram of the de-excitation processes of atomic core holes. a) X-ray emission. b) Auger electron emission. 28
1.10 An Auger spectrum of contaminated copper showing the total energy distribution and its first derivative. 30
2.1 The Varian 240 vacuum chamber and its associated hardware.

2.2 Pump and gas line configuration for the Varian 240 Vacuum chamber.

IG = Ion Gauge, TCG = Thermocouple Gauge

2.3 Schematic diagram of the laser method used to check correspondence of the optical and crystallographic planes.

2.4 Configuration of the LEED optics for use as a retarding field analyzer (RFA) for Auger electron spectroscopy (AES).

2.5 Simplified diagram of the LEED optics used for displaying diffraction patterns.

2.6 Block diagram of the video LEED analyzer (VLA).

2.7 I(E) curves for symmetrically related beams from Cu(110)-(2x1)-O and Cu(311) surfaces. These equivalent beams are averaged, smoothed, and if needed, the background is subtracted.

2.8 LEED spot profile analysis: a) a user selected (10x10) pixel window is placed over the diffraction spot b) a LEED spot profile - the FWHM gives a measure of spot sharpness.

3.1 a) The real space ideal bulk truncation representation of f.c.c.(311)
b) The reciprocal space f.c.c.(311) net (LEED pattern).

3.2 Auger spectra of the Cu(311) surface.

a) Prior to cleaning in UHV.

b) After cleaning by argon ion bombardment/anneal cycles.

3.3 Experimental I(E) curves recorded for the clean Cu(311) surface.

a) (1,-3) and (-1,-2) beams at normal incidence.

b) (1,-2) and (-1,-1) beams at normal incidence.

c) (1,-1) and (-1,0) beams at normal incidence.
d) (1,0) and (-1,1) beams at normal incidence. 56

e) (1,1) and (-1,2) beams at normal incidence. 57

f) (1,2) and (-1,3) beams at normal incidence.

g) (0,-3) beam at normal incidence.

h) (0,-2) beam at normal incidence.

i) (0,-1) beam at normal incidence. 58

j) (0,2) beam at normal incidence.

k) (0,1) beam at normal incidence. 59

l) (0,3) beam at normal incidence.

m) (2,-2) and (-2,0) beams at normal incidence.

n) (2,-1) and (-2,1) beams at normal incidence. 60

o) (1,-3) and (-1,-2) beams at 10° off normal incidence.

p) (1,-2) and (-1,-1) beams at 10° off normal incidence.

q) (1,0) and (-1,1) beams at 10° off normal incidence. 61

r) (0,-3) beam at 10° off normal incidence.

s) (0,2) beam at 10° off normal incidence.

t) (0,0) beam at 10° off normal incidence. 62

3.4 Auger peak height ratio $R = \frac{S(152eV)}{Cu(920eV)}$ plotted as a function of $H_2S$ exposure time at $2 \times 10^{-8}$ torr. 64

3.5 Photographs of the LEED pattern for sulphur adsorbed on Cu(311)

a) 62eV  b) 67eV  c) 76eV  d) 142eV  66

3.6 Adsorption of Sulphur on the Cu(311) surface.

a) The two equivalent adsorption sites between adjacent terraces.

b) Possible arrangements of sulphur on Cu(311) giving (2x1) patterns.

c) Possible (2x3) arrangements of sulphur on Cu(311). 69
d) Possible (2x5) arrangements of sulphur on Cu(311).

4.1 a) A real space ideal bulk truncation representation of the f.c.c.(110) surface.

b) The reciprocal space f.c.c.(110) net (LEED) pattern.

c) The LEED pattern of the Cu(110)-(2x1)-O adsorption system.

4.2 Proposed models for the Cu(110)-(2x1)-O surface.

a) Unreconstructed.  

b) Buckled row.

c) Missing row  

d) Sawtooth.

4.3 Normalised $1/\text{FWHM}$ of the $(-1/2,1)$ and $(-1/2,-1)$ fractional beams from the Cu(110)-(2x1)-O surface plotted as a function of exposure time to oxygen at 4x10^-8 torr.

4.4 Experimental I(E) curves recorded for the Cu(110)-(2x1)-O surface.

a) (0,1) and (0,-1) beams at normal incidence.

b) (1,1),(1,-1),(-1,1) and (-1,-1) beams at normal incidence.

c) (2,0) and (-2,0) beams at normal incidence.

d) (2,1),(2,-1),(-2,1) and (-2,-1) beams at normal incidence.

e) $(1,1/2),(1,-1/2),(-1,1/2)$ and $(-1,-1/2)$ beams at normal incidence.

f) $(2,1/2),(2,-1/2),(-2,1/2)$ and $(-2,-1/2)$ beams at normal incidence.

g) $(0,1/2)$ and $(0,-1/2)$ beams at normal incidence.

h) $(0,3/2)$ and $(0,-3/2)$ beams at normal incidence.

i) $(1,3/2),(-1,3/2),(1,-3/2)$ and $(-1,-3/2)$ beams at normal incidence.

j) $(-1,1)$ and $(-1,-1)$ beams at 10° off normal incidence.

k) (0,1) and (0,-1) beams at 10° off normal incidence.

l) $(-1,0)$ beam at 10° off normal incidence.

m) $(-2,0)$ beam at 10° off normal incidence.
4.4  n) (0,2) and (0,-2) beams at 10° off normal incidence.
   o) (0,0) beam at 10° off normal incidence.
Acknowledgements

Throughout the course of my study at UBC, I have appreciated the interest and advice of my research supervisor, Prof. K.A.R. Mitchell, as well as his comments on and careful reading of this thesis.

I would like to acknowledge the members of the surface science group past and present at UBC. Special thanks are due to Dr. R.A. McFarlane for introducing me to the experimental aspects of LEED, and Mr H.C. Zeng for his many useful suggestions on parts of this work. I also acknowledge Mr J.R. Lou, Dr P.C. Wong, Ms Y.K. Wu, and latterly Mrs T.V. Grimsby and Prof. M.Y. Zhou.

I am indebted to many members of the mechanical and electronics workshops, without whose assistance, the running and maintenance of the vacuum system and its auxiliary hardware would have been far from pleasant.

Finally, I would like to thank my parents and my girlfriend Stephanie, to whom I dedicate this thesis.
Chapter 1

An Introduction to Low Energy Electron Diffraction
1.1 Modern Surface Science

The study of surface physico-chemical properties has seen a dramatic shift in emphasis over the last few decades from the investigation of 'real' or polycrystalline dirty surfaces to the examination of clean single crystal surfaces. This change was due to a realisation that knowledge of fundamental surface properties could best be achieved by an understanding of ordered, clean surfaces.

The modern approach to surface science has been facilitated in the last 25 years by the ability to routinely attain ultrahigh vacuum (UHV, pressure <10^{-9} torr), essential for maintaining surface cleanliness. In addition, the proliferation of surface sensitive techniques developed in the interim have provided access to a wide range of relevant information, which in turn has led to important advances in materials science [1,2,3]. Some of the more common techniques are listed in table 1.1.

Structural geometry and elemental composition are of paramount importance in surface science. Most work has concentrated on the low Miller index surfaces of metals and semiconductors, due in part to their close packed natures and high degrees of symmetry. On the other hand, 'real' surfaces used as heterogeneous catalysts for example, include a variety of crystal faces, exhibiting many stepped surfaces. Indeed it is these steps that are thought to be the 'active sites' in such catalysts [4], and so structural analyses of high Miller index surfaces and of adsorption on them are essential.

The combination of low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) has been particularly significant in surface characterization. Surface crystallography using LEED is now a mature science, such that the types of surface that can be studied with confidence grows continually. There is already a sizeable database of several hundred surface structures that have been 'solved' by
<table>
<thead>
<tr>
<th>Technique</th>
<th>Acronym</th>
<th>Probe Particle</th>
<th>Detected Particle</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auger Electron Spectroscopy</td>
<td>AES [7,9]</td>
<td>electron</td>
<td>electron</td>
<td>Elemental composition</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy</td>
<td>XPS [9]</td>
<td>photon</td>
<td>electron</td>
<td>Composition, electronic states</td>
</tr>
<tr>
<td>Angle Resolved X-ray Photoelectron Spectroscopy</td>
<td>ARXPS [12]</td>
<td>photon</td>
<td>electron</td>
<td>Geometrical structure, composition</td>
</tr>
<tr>
<td>Grazing Incidence X-ray Scattering</td>
<td>GIXS [14]</td>
<td>photon</td>
<td>photon</td>
<td>Geometrical structure</td>
</tr>
<tr>
<td>Surface Enhanced Raman Spectroscopy</td>
<td>SERS [16]</td>
<td>photon</td>
<td>photon</td>
<td>Vibrational modes</td>
</tr>
<tr>
<td>Helium Atom Diffraction</td>
<td>HEAD [17]</td>
<td>atom</td>
<td>atom</td>
<td>Geometrical structure</td>
</tr>
<tr>
<td>Impact-Collision Ion Scattering Spectroscopy</td>
<td>ICISS [18]</td>
<td>ion</td>
<td>ion</td>
<td>Geometrical structure, composition</td>
</tr>
<tr>
<td>High/Low Energy Ion Scattering Spectroscopy</td>
<td>HEIS/LEIS [19]</td>
<td>ion</td>
<td>ion</td>
<td>Geometrical structure, composition</td>
</tr>
<tr>
<td>Secondary Ion Mass Spectrometry</td>
<td>SIMS [20]</td>
<td>ion</td>
<td>ion</td>
<td>Composition</td>
</tr>
<tr>
<td>Scanning Tunneling Microscope</td>
<td>STM [21]</td>
<td>electric field</td>
<td>tunneling current</td>
<td>Geometrical, defect and electronic structures</td>
</tr>
</tbody>
</table>
LEED, so much so that it has been frequently used to assess the capability and potential of other, newer surface structure probes.

1.2 Classification of Surface Structures

1.2.1 The Step and Microfacet Notations for Stepped Surfaces

Single crystal surfaces can be classified by the Miller indices of the corresponding bulk crystallographic planes. In surface crystallography, reference to 'low' and 'high' Miller indices is frequently made. The low Miller index faces of cubic crystals are the (111), (100) and (110) faces. The term 'high Miller index' is taken to mean surfaces containing step and terrace structure where the terraces are not too large. As one goes to higher and higher Miller indices, the surface will resemble the low Miller index surface of its terrace planes, both chemically and physically. For example, a surface whose Miller indices are (400,1,1) could equally well be thought of as a (100) surface, misaligned by ~0.2°, which was the allowed misalignment error in this work (see section 2.2). This is adequate for the low Miller index surfaces, but for high Miller index surfaces, no indication of step or terrace structure is given. The simplest stepped surfaces have low Miller index terraces of fixed width and low Miller index steps of single atom height. The second type have steps of high Miller index, such that the steps have steps, and are known as 'kinked' surfaces. The step notation of Lang et al [22] classifies a stepped surface as

\[(hkl) = n(h_1k_1l_1)x(h_2k_2l_2)\]
where \( n \) is the number of rows of atoms per terrace and \((h_1k_1l_1),(h_5k_5l_5)\) are the Miller indices of terrace and step planes respectively. In some cases, for example the face centered cubic (f.c.c.) (311) surface, there is no unique step notation, since it could be written as \(2(100)x(111)\) or \(2(111)x(100)\) depending on how the surface is viewed.

The step notation is adequate for simple stepped surfaces, but for kinked surfaces, no provision is made for the further breakdown of the step indices. A more serious drawback in the case of kinked surfaces is that \( n \) must be non-integral, otherwise its value depends on which row of atoms is counted. In either case, \( n \) cannot be easily recognised from the Miller indices.

The microfacet notation for cubic crystals, introduced by Van Hove and Somorjai [23] relies on the \((hkl)\) plane being perpendicular to the \((hkl)\) vector. This vector can be split into three linearly independent vectors \((h_1k_1l_1),(h_2k_2l_2),(h_3k_3l_3)\). Any high Miller index plane \((hkl)\) may then be written as

\[
(hkl) = a_x(h_1k_1l_1) + b_y(h_2k_2l_2) + c_z(h_3k_3l_3)
\]

where the coefficients \(a, b, c\) are the relative amounts of each component vector, and the subscripts \(x, y, z\) give the number of unit meshes of \((h_1k_1l_1)\) per unit mesh of \((hkl)\). For simple stepped surfaces, only the first two terms are needed. Examples of these nomenclatures are given in table 1.2. Like the step notation, there is no single microfacet notation for a given surface. It depends on which microfacets are chosen to break the surface down into, the best choice of which may vary depending on the application.
Table 1.2 Examples of the step and microfacet notations for some f.c.c. stepped surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Miller</th>
<th>Step</th>
<th>Microfacet</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Surface" /> (533)</td>
<td>4(111)x(100)</td>
<td>3_3(111)+2_1(100)</td>
<td></td>
</tr>
<tr>
<td><img src="image2.png" alt="Surface" /> (911)</td>
<td>5(100)x(111)</td>
<td>8_4(100)+1_1(111)</td>
<td></td>
</tr>
<tr>
<td><img src="image3.png" alt="Surface" /> (775)</td>
<td>7(111)x(111)</td>
<td>5_5(111)+2_1(110)</td>
<td></td>
</tr>
<tr>
<td><img src="image4.png" alt="Surface" /> (1087)</td>
<td>7(111)x(310)</td>
<td>7_14(111)+1_1(110) +2_2(100)</td>
<td></td>
</tr>
</tbody>
</table>
1.2.2 The Unit Mesh and Reciprocal Net

The diperiodicity of a single crystal surface means that each pair of equivalent points can be related by a translation vector

\[ \mathbf{t} = m\mathbf{a}_1 + n\mathbf{a}_2 \]

The unit vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) define a unit mesh (in analogy with the unit cell of X-ray crystallography), which with the set of integers \( \{m,n\} \) generate a net analogous to the lattice of triperiodic crystallography. A diffraction pattern is a direct representation of the surface net in reciprocal space. It is defined by vectors \( \mathbf{a}_1^\ast \) and \( \mathbf{a}_2^\ast \) such that

\[ \mathbf{a}_i \mathbf{a}_j^\ast = 2\pi \delta_{ij} \]

where the Kronecker symbol, \( \delta_{ij} = 0 \) if \( i \neq j \) and \( \delta_{ij} = 1 \) if \( i = j \).

These unit vectors describe the reciprocal net according to

\[ \mathbf{g} = h\mathbf{a}_1^\ast + k\mathbf{a}_2^\ast \]

where \( h, k \) are integers.

There are five Bravais unit meshes, analogous to the fourteen Bravais unit cells of bulk crystallography. These are shown in both real and reciprocal space in figure 1.1. Details of the various conventions in surface crystallography are given in the International Tables for X-ray Crystallography [24], and in an article by Wood [25].
Figure 1.1 The five Bravais two-dimensional meshes in real and reciprocal space.
1.2.3 Overlayer Structures - Wood and Matrix Notations

Miller indices, or the step and microfacet notation, may not be sufficient to describe the translational symmetry of a surface completely. The diperiodicity of the surface can be altered by reconstruction of the topmost atomic layer(s) and/or by adsorption, resulting in extra diffraction spots if the overlayer unit mesh is larger than the substrate unit mesh. To relate the unit meshes, two naming schemes have been developed, Wood notation and matrix notation. The Wood notation [25] designates the superlattice structure as

\[
\begin{pmatrix}
|S_1| & |S_2| \\
|\mathbf{a}_1| & |\mathbf{a}_2|
\end{pmatrix} \Theta X
\]

where \(\mathbf{a}_1, \mathbf{a}_2\) and \(S_1, S_2\) are the vectors which describe the unit meshes of the substrate and surface structures respectively, \(\Theta\) gives the rotation angle between the meshes (dropped if \(\Theta = 0\)) and \(X\) denotes the adsorbed species. The expression is sometimes prefixed by a 'c' or 'p' to denote centered or primitive meshes respectively. Wood notation can only be applied if the angle between \(\mathbf{a}_1\) and \(\mathbf{a}_2\) is the same as that between \(S_1\) and \(S_2\). In cases where these angles are different, the more general matrix notation [26,27] must be used. It gives the relationship between the surface region probed by LEED and the substrate as

\[
\begin{pmatrix}
S_1 \\
S_2
\end{pmatrix}
= \begin{pmatrix}
\mathbf{a}_{11} & \mathbf{a}_{12} \\
\mathbf{a}_{21} & \mathbf{a}_{22}
\end{pmatrix}
\begin{pmatrix}
\mathbf{a}_1 \\
\mathbf{a}_2
\end{pmatrix}
= \mathbf{A}_{\mathbf{a}}
\]
and the determinant of $A$ gives the size of the superlattice mesh with respect to the substrate mesh. Some examples of the Wood and matrix notations are given in figure 1.2.

1.3 Low Energy Electron Diffraction

The origins of LEED can be traced back to experiments performed in 1927 by Davisson and Germer [28], who first observed the diffraction of low energy electrons and recognized their inherent surface sensitivity. Development of the technique however was hampered by experimental and theoretical difficulties, so that surface structure determination was not possible until the early 1970's. The experiment essentially consists of directing a monoenergetic, collimated electron beam in the 10-300eV range at a surface and studying the elastically backscattered electrons. These electrons are usually collected on a fluorescent screen, though there are alternative collection devices [5]. In the conventional display systems, if the surface is well ordered, a pattern of spots is produced whose arrangement and sharpness is governed by the ordering of the surface.

1.3.1 Electron Scattering

Low energy electrons have wavelengths which, according to de Broglie's hypothesis

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda(\text{Å}) = \left( \frac{150.4}{E(\text{eV})} \right)^{1/2}$$
Wood and matrix notation for some overlayer structures on the f.c.c.(110) surface.

- fcc(110) (1x1) 
  - e.g. clean surface

- fcc(110) (2x1)
  - e.g. Cu(110) (2x1) O
  - Ir(110) (2x1)

- fcc(110) (2x2)
  - e.g. Cu(110) (2x2) Au
  - Cu/Ni(110) (2x2) CO

- fcc(110) c(2x2)
  - e.g. Ni(110) c(2x2) CO
  - Pt(110) c(2x2) O

Figure 1.2 Wood and matrix notation for some overlayer structures on the f.c.c.(110) surface.
are of the same order as atomic spacings in solids. As such, constructive and destructive interference would be expected to produce a diffraction pattern containing structural information upon interaction with an ordered crystal surface.

An energetically well defined electron beam (energy $E_p$) incident on a surface will give rise to backscattered and secondary electrons. There are three distinct regions in the energy distribution as shown in figure 1.3. LEED depends on electrons in region I, that is the elastically and 'quasi-elastically' scattered electrons (those having suffered small ($<0.1\text{eV}$) energy losses via phonon interaction) which constitute a few percent of the total incident electrons. Region II contains peaks due to Auger electrons and plasmon losses superimposed on a general scattered background [29], and region III is made up of the 'true secondary' electrons, those having undergone a series of inelastic scattering events [8]. The surface sensitivity of LEED is a direct result of the high probability of inelastic scattering for low energy electrons. This dictates that $L$, the mean free path of an electron in a solid, defined by

$$L = l_0 \exp \left(-\frac{l}{L} \right) \quad 1.9$$

is of the order of a few atomic layer spacings. In equation 1.9, $l_0$, the incident beam intensity is attenuated to $l$ after passage through a distance $l$ within the crystal. The mean free path of an electron in a metallic solid, as a function of energy is shown in figure 1.4.
Figure 1.3 A typical energy distribution of backscattered electrons as a function of the primary beam energy $E_p$.

Figure 1.4 Typical energy dependence of electron mean free path, $L$, in a metallic solid.
1.3.2 Conditions for Elastic LEED

In a LEED experiment, the electron beam impinges on a surface with direction \((\theta, \phi)\) as shown in figure 1.5. Outside the influence of a crystal, the incident and back diffracted electrons experience a field free region, where they can be expressed as plane waves

\[ \Psi_k(r) = \exp(ik \cdot r) \quad 1.10 \]

where the wavevector \( k \) specifies the direction of the beam and relates to wavelength according to

\[ |k| = \frac{2\pi}{\lambda} \quad 1.11 \]

and energy by

\[ E = \frac{\hbar^2 |k|^2}{2m} \quad 1.12 \]

where \( m \) = electron mass and \( \hbar = \frac{\hbar}{2\pi} \).

For incident and diffracted beams with wavevectors \( k_0 \) and \( k' \), the differential scattering cross section is

\[ \left( \frac{d\sigma}{d\Omega} \right) = \left( \frac{m}{2\pi\hbar^2} \right)^2 |\langle k' | T | k_0 \rangle|^2 \quad 1.13 \]
Figure 1.5 The geometry of the LEED experiment; an electron beam is incident on the surface with an energy $E$ and direction $(\theta, \phi)$. The intensity of the diffracted beam is recorded as a function of $E$. 
where $T$ is the transition operator. This cross section gives a measure of the number of electrons scattered per unit time per unit solid angle in the direction $k'$ for a unit incident flux in direction $k_0$. For a symmetry operation $S$ applied to the surface, the matrix element above satisfies [30,31,32]

$$\langle k'|T|k_0 \rangle = \langle k'|S^{-1}TS|k_0 \rangle = \langle Sk'|T|Sk_0 \rangle$$  \hspace{1cm} 1.14

If $S$ is a translation by a surface net vector $\mathbf{t}$, then the two ends of equation 1.14 give

$$\langle k'|T|k_0 \rangle = \exp[i(k_0 - k') \cdot t] \langle k'|T|k_0 \rangle$$  \hspace{1cm} 1.15

This equation is satisfied if $\langle k'|T|k_0 \rangle = 0$, corresponding to zero scattered intensity, or when

$$\exp[i(k_0 - k') \cdot t] = 1$$  \hspace{1cm} 1.16

Since the surface net vector $\mathbf{t}$ has the form

$$\mathbf{t} = m\mathbf{s}_1 + n\mathbf{s}_2$$  \hspace{1cm} m,n = integers  \hspace{1cm} 1.17

where $\mathbf{s}_1, \mathbf{s}_2$ are the real space unit mesh basis vectors, equation (1.16) will be satisfied whenever the parallel component of the difference of the incident and diffracted wavevectors equals a vector of the reciprocal net

$$\mathbf{g} = k_0 \parallel k_\parallel' = h\mathbf{s}_1^* + h\mathbf{s}_2^*$$  \hspace{1cm} h,k = integers  \hspace{1cm} 1.18
and since \( \mathbf{t} \) is parallel to the surface, the dot product of \( \mathbf{t} \) with the components of \( \mathbf{k}_0 \) and \( \mathbf{k}' \) perpendicular to the surface will be zero, giving the diffraction condition

\[
\exp[i(\mathbf{k}_0 \cdot \mathbf{t} - \mathbf{k'} \cdot \mathbf{t})] = 1
\]

which is met if

\[
(hb_1 + kb_2) \cdot (mb_1 + nb_2) = 2\pi \text{(integer)}.
\]

Applying equation 1.4 gives

\[
2\pi(hm + kn) = 2\pi \text{(integer)}
\]

and this condition holds if the parallel components of the wave vectors satisfy

\[
\mathbf{k}'_{\parallel} = \mathbf{k}_0_{\parallel} + \mathbf{q}(h,k) \quad h,k \text{ = integers}
\]

The superscripts (+/-) denote wavevector direction into/out of the crystal, and \( \mathbf{q}(h,k) \) are vectors of the reciprocal net. Equation (1.22) is simply a statement of momentum conservation parallel to the surface. It, along with the energy conservation condition (elastic scattering), namely

\[
|\mathbf{k}_0^-|^2 = |\mathbf{k}_0^+|^2
\]

defines the diperiodic diffraction condition in LEED.
The indices \((h,k)\) are commonly used to label the diffracted beams. Equation (1.22) shows that the specular \((0,0)\) beam is formed by electrons that have interacted with the surface without momentum transfer parallel to the surface, therefore its direction is independent of energy. Non-specular beams however, will tend to converge on the specular beam with increasing energy. This can be seen by adapting the Ewald sphere \([5]\) from X-ray diffraction to the diperiodic case of LEED as shown in figure 1.6. The intersection of this sphere with the reciprocal lattice rods define the conditions under which both the parallel momentum and energy conservation requirements are simultaneously met.

1.3.3 Surface Crystallography by LEED

As with X-ray diffraction, a full structural analysis by LEED cannot be effected simply by knowledge of the diffraction pattern, as evidenced by figure 1.7. To extract structural information, the spot intensities at varying incident electron energies are recorded as intensity versus energy or \(I(E)\) curves. The experimental \(I(E)\) curves are then matched to theoretical \(I(E)\) curves calculated for various 'model' structures. The model which gives the best agreement between theory and experiment is deemed to be the closest to the actual structure.

A LEED experiment is restricted by instrumental limitations associated with energy and angular deviations in the electron beams. Park et al \([33]\) have defined an instrument response function which yields a characteristic dimension, the transfer width \(W\). For conventional systems, this is typically about \(100\,\text{Å}\) and it represents the limit over which structural features can be detected \([34]\). For a surface whose domain dimensions are greater than \(W\), observed LEED patterns are made up of superimposed diffraction patterns from many regions of approximate area \(W^2\). When there are
Figure 1.6  The Ewald sphere construction for LEED. The Ewald sphere is shown at two energies for the same incident direction (view parallel to the surface).
Figure 1.7 Five types of adatom structure on the f.c.c.(110) surface. Each would produce a (2x1) diffraction pattern, illustrating that the structural analysis requires more than just knowledge of the diffraction pattern.
ordered regions on the surface of this magnitude, the LEED patterns observed will be as sharp as possible for that particular instrument. Imperfections between these ordered regions will contribute to the general background scattering but will not affect the beam sharpness [34].

Some surfaces can exhibit ordered regions that are related by a symmetry operation. With these symmetrically related 'domains', of the types illustrated in figure 1.8, the observed LEED pattern represents a sum of diffraction patterns from the individual domains. A consequence is that the diffraction pattern then appears with the point group symmetry of the substrate rather than that of a local ordered region of the surface.

1.3.4 Calculation of LEED Intensities

The strong interaction of slow electrons with solids, caused by the large scattering cross section, precludes the use of a single scattering theory as used in X-ray diffraction. The high probability that electrons will scatter several times before leaving the surface requires a multiple scattering, or dynamical theory of electron diffraction to interpret the structure in experimental I(E) curves. Since the interaction is so strong, it is clear that the scattering potential should be well chosen. The usual approach is to follow band structure theories [35] and approximate a solid's potential with the 'muffin tin' model. This model assumes that the potential within each atom is spherically symmetric, and that the potential between atoms is a constant \( V_0 \), such that

\[
V_0 = V_{0r} + iV_{0i}. \tag{1.24}
\]
(2x1) domains on f.c.c.(311) related by a mirror reflection

(2x1) domains on f.c.c.(110) related by a translation operation

(2x1) domains on f.c.c.(100) related by a 90° rotation

Figure 1.8 Three types of domain structure found for overlayers on f.c.c. crystal faces.
The real component, $V_{or}$, often loosely termed the 'inner potential', accounts for the lowering in potential energy experienced by an electron on entering the solid and is typically between -5 and -15 eV. The imaginary component, $V_{oi}$, also a negative quantity, accounts for energy damping due to inelastic scattering, and is usually treated as a constant, though sometimes it is given a weak energy dependence (e.g. as $E^{1/3}$ [36]).

The salient features of any multiple scattering formalism are as follows: The incident electron beam, treated as a plane wave of the form $\exp(ikr)$, interacts with the surface and is scattered by individual atoms. These scattered waves interact with each other and with the primary electron beam to produce an effective electron wave which scatters further. This process can be envisaged to continue until the resulting effective electron wave becomes self-consistent, thereby allowing the diffracted beam intensities to be calculated. The treatment of this overall scattering problem is broken into simpler parts. First consideration is for the scattering by the spherical potentials of the individual atoms, atoms are then built up into layers, and the scattering by a layer is calculated, and finally the layers are stacked. Exact solutions to the interlayer scattering involve calculations to infinite order in either K-space using the Bloch wave method [37,38] or in L-space by the T-matrix method [39]. The high cost in computer time and storage of these exact solutions led to the development of perturbative schemes that effectively speed up the calculations. These methods rely on the inelastic energy damping to limit the number of multiple scattering events [5].

A multiple scattering analysis of the Cu(311) I(E) data presented in this thesis is being carried out using the so called 'layer doubling' method developed by Pendry [40-42]. This method starts with the scattered amplitudes due to multiple scattering in two individual layers. These layers are then stacked together and expressions are derived to
calculate the scattering from the two layers together. This procedure is then continued such that each iteration doubles the number of layers from the previous iteration, and the resulting reflection matrices converge due to the small electron mean free path, typically on the third or fourth iteration (8 or 16 atomic layers). These bulk reflections can be stored and re-used with varying structural parameters such as the interlayer spacing. The layer doubling method is efficient and flexible, though convergence may fail if interlayer spacings are less than around 0.6Å.

Other perturbational schemes include renormalised forward scattering (RFS) [43] and the combined space method (CSM) [41,44]. In RFS, backscattering of electrons, which is usually weak compared to forward scattering, is treated perturbationally while the latter is calculated exactly. In the first-order calculation, all scattering paths from single back scattering processes are considered, while the second and third order calculations have three and five back reflections respectively. The iteration continues until the sum of the amplitudes of the beams forward scattered into the crystal has dropped to a small predetermined fraction (~0.3%) of the incident beam amplitude, which typically requires twelve to fifteen layers.

When interlayer spacings are small, the number of plane waves (beams) needed for calculation becomes large, this increases the size of the diffraction matrices. The problem can be overcome using L-space methods which are more efficient for small interlayer spacings. In the CSM, small interlayer spacings resulting from ad-atoms for example are treated in the L-space representation, and the K-space representation is used for the main part of the crystal where interlayer spacings are sufficiently large.
1.3.5 Evaluation of LEED I(E) Curves

Structure determinations by LEED are carried out by comparison of experimental I(E) curves with those calculated for a number of plausible models. The evaluation is done both visually and mathematically by the use of reliability indices or R-factors. An R-factor is a dimensionless number that decreases as the correspondence between curves improves, such that \( R \to 0 \) as \( I_t(E) \to I_e(E) \). There are currently at least ten R-factors used in LEED crystallography, each is sensitive to different features of the I(E) curves [5]. The analysis of the Cu(311) I(E) curves presented in chapter 3 will utilize three of these, which are now briefly described.

The R-factor \( R_2 \) [45] is sensitive to relative peak heights in the I(E) curves, and is defined as

\[
R_2 = A_2 \int (I_e - cI_t)^2 dE
\]  \hspace{1cm} (1.25)

where \( I_e \) and \( I_t \) are experimental and theoretical intensities respectively, and the constant \( c \), given by

\[
c = \frac{\int I_e dE}{\int I_t dE}
\]  \hspace{1cm} (1.26)

serves to normalise the two curves, and the prefactor \( A_2 \), given by

\[
A_2 = \frac{1}{\int I_e^2 dE}
\]  \hspace{1cm} (1.27)
normalises $R^2$ and renders it dimensionless.

The Zanazzi-Jona R-factor [45,46] is sensitive to the general shape of the $I(E)$ curves and attempts to quantify all features evaluated in a visual comparison. For a single beam, Zanazzi and Jona have proposed

$$r_{ZJ} = A_{ZJ} \frac{|I_e'' - cI_e'| |I_e' - cI_e'|}{|I_e'| + \max |I_e'|} \quad 1.28$$

where

$$A_{ZJ} = \frac{1}{0.027 \int I_0 dE} \quad 1.29$$

and

$$c = \frac{\int I_0 dE}{\int I_1 dE} \quad 1.30$$

is a scaling constant; the single and double primes represent first and second derivatives of intensity with respect to $E$. The many beam Zanazzi-Jona R-factor is defined by

$$R_{ZJ} = \frac{\sum_i r_{ZJ} \Delta E_i}{\sum_i \Delta E_i} \quad 1.31$$
where $i$ runs over all the individual beams and $\Delta E^i$ is the energy range of the $i^{th}$ beam.

The R-factor proposed by Pendry uses the derivative of the logarithm of the intensities of $I(E)$ curves, and is sensitive to relative peak positions. The Pendry multibeam R-factor [45,47] is defined as

$$R_{Pe} = \frac{\sum_i (Y_e^i - Y_t^i)^2 dE}{\sum_i (Y_e^{i2} + Y_t^{i2}) dE}$$

where

$$Y = \frac{L^{-1}}{L^{-2} + V_{oi}^2}$$

and

$$L = \frac{d\ln I(E)}{dE}$$

$V_{oi}$ is the imaginary component of the muffin-tin constant potential used in the multiple scattering calculations.

### 1.4 Auger Electron Spectroscopy

Routine surface composition analysis under UHV was not possible until the availability of Auger electron spectroscopy [7] in the late 1960's. The phenomenon was named after Pierre Auger who first observed and correctly interpreted it in 1925 [48]. The process is schematically depicted in figure 1.9; its first step involves
Figure 1.9
Schematic diagram of the de-excitation processes of atomic core holes.

a) X-ray emission.

b) Auger electron emission.
ionization by either electron, photon or ion impact of an inner electronic energy level to form a core 'hole'. The system will then relax by an outer electron dropping into the core hole. The excess energy may be released either by X-ray emission, or by transference to a third electron (the 'Auger' electron) which leaves the atom with a kinetic energy characteristic of the element concerned. Thus AES can be used to identify all elements, with the exception of hydrogen and helium.

The surface sensitivity of AES stems from the short mean free paths of electrons with energy in the 50-1000eV range (figure 1.5). Auger electrons tend to be accompanied by a large, slowly varying background of secondary electrons; as a consequence Auger electron spectra are Conventionally viewed as a plot of the first derivative of the number of electrons versus energy. Figure 1.10 is an example of an Auger spectrum of contaminated copper from this work showing the energy distribution spectrum and its first derivative. Identification of peaks in an Auger electron spectrum is accomplished by comparing the peak position (taken by convention to be the position of the minimum in the derivative peak) to either standard spectra [49], or to tables of Auger emission energies [50]. Estimates of the relative amounts of an element on a surface can be provided by the ratio of an adsorbate AES peak height to that for a substrate peak. Absolute quantitative analysis requires a suitable calibration against a standard sample or some other technique, such as radiotracer analysis [9].
Figure 1.10 An Auger spectrum of contaminated copper showing the total energy distribution and its first derivative.
Chapter 2

Experimental Methods
2.1 Vacuum Chamber and Pumpdown

The experiments in this work were performed in a Varian 240 vacuum chamber made of demagnetized stainless steel. The various components are connected by knife edge flanges with copper gaskets. Figure 2.1 shows front and side views of the chamber, which is equipped with conventional hemispherical 4-grid LEED optics (Varian 981-0127) which also act as a retarding field analyzer for AES. Other facilities include an argon ion bombardment gun (Varian 981-1045) for sample cleaning, a nude ion gauge (Varian 971-0003) for pressure measurement and a molybdenum sample holder with a resistive heater (Varian 981-2058) and 0.005 inch chromel-alumel thermocouple wires mounted on a high precision manipulator (Varian 980-0523). The manipulator and sample holder keep the surface at the focus of the LEED screen and allow sample translation in three dimensions and rotation about two perpendicular axes. Stray magnetic fields are neutralized by mutually orthogonal Helmholz coils [6,51].

The argon used in the cleaning procedures, and the gases for chemisorption experiments are admitted into the chamber through a variable leak valve (Varian 951-5106) via a nozzle from the gas line. The gas line is bakeable separately from the main chamber and has its own small 20 ls\(^{-1}\) ion pump (Varian 981-0200). Pressure in the gas line is monitored with two thermocouple gauges (Varian 972-0006) and the gauge on the small ion pump control unit.

Ultrahigh vacuum is achieved by a combination of pumps as shown in figure 2.2. Rough pumping from atmospheric pressure down to the 10\(^{-2}\) torr range, is achieved by the liquid nitrogen cooled sorption pump. The liquid nitrogen trapped, water cooled oil diffusion pump (Varian M2) then takes the chamber into the 10\(^{-7}\) torr range. At this stage, the system is baked at \(\sim180^\circ\text{C}\) for 15-20 hours with the main ion pump (200 ls\(^{-1}\)) on to remove gases adsorbed on the inside of the chamber. After
Figure 2.1 The Varian 240 vacuum chamber and its associated hardware.
Figure 2.2 Pump and gas line configuration for the Varian 240 vacuum chamber.

IG = Ion Gauge, TCG = Thermocouple Gauge
bakeout, all the filaments are degassed while the chamber is still hot. On cooling, the pressure in the chamber is around $2 \times 10^{-10}$ torr, this degree of UHV can be maintained by periodic use of the titanium sublimation pump.

2.2 Sample Preparation and Cleaning

The copper (311) and (110) samples used in this study were prepared from a 99.999% pure single crystal rod (grown by A. Akhtar, Dept. of Metallurgy, University of British Columbia). The crystal was mounted on a goniometer and oriented using the Laue back reflection method [52]. After orientation a slice of about 1mm thickness was cut by the spark erosion technique ('Agietron', Agie, Switzerland) parallel to the desired crystallographic plane. The sample was set in an acrylic resin ('Quickmount', Fulton Metallurgical Products Corp., USA) and glued to a polishing jig equipped with alignment micrometers. This jig was placed on a planetary lapping polisher (DU 172, Canadian Thin Film Ltd.), and polished with 9µm and 6µm diamond pastes and the orientation was re-checked. The sample was then hand polished with 3µm and 1µm diamond pastes on artificial deerskin (Buehler microcloth 40-7218). After polishing to optical flatness, the jig was fixed on an optical bench and a He/Ne laser was used to ensure that the optical face and the desired plane were within 0.2°, as shown in figure 2.3. Upon satisfactory orientation, the resin was dissolved in acetone and the sample was degreased in trichloroethylene and washed consecutively in acetone, methanol and distilled water. When dry, the crystal was mounted on the manipulator and the thermocouple wires were spot welded to the sample cup. The manipulator was placed inside the vacuum chamber, and the system was pumped down as described in the preceding section.
Figure 2.3 Schematic diagram of the laser method used to check correspondence of the optical and crystallographic planes.
The main impurities on both surfaces were carbon, chlorine and sulphur as determined by AES. Surface cleaning within UHV was achieved by sputter-etching with argon ions. Initially \( \sim 5 \times 10^{-5} \) torr of argon was admitted into the chamber. These argon atoms were then ionized by electrons from a hot filament and accelerated toward the earthed sample by a potential of 400V with a current density of 2.0\( \mu \text{A/cm}^2 \). Atoms thus sputtered from the surface were removed using the TSP which has a negligible pumping speed for the rare gases. After 2 hours, the bombardment was stopped and the argon was pumped away with the diffusion pump and the main ion pump. This initial gentle bombardment was followed by an anneal for 15 minutes at 550°C and was sufficient to remove most of the surface contaminants left over from the preparation and cleaning procedures outside of UHV. Subsequent cleaning was done with a higher argon ion gun potential of 590V for 2-4 hours, with anneals up to 650-700°C for 10-15 minutes. AES showed that carbon and chlorine were removed fairly easily, but the high temperature anneal caused sulphur to segregate from the bulk. Many hours of bombard-anneal cycles were needed before the bulk region close to the surface was depleted of sulphur to the extent that the surface sulphur contamination was below the detection limit of the RFA, and hence of the order of 1-2% of a monolayer [53]. As the surfaces became cleaner and more ordered, the annealing temperature was lowered somewhat to around 550-600°C. The cleaned surfaces then gave sharp (1\times1) LEED patterns, with low background, free of fractional beams and streaks.

2.3 AES for Surface Composition Analysis

In this work, AES was used to qualitatively monitor the surface composition with the LEED optics acting as a RFA [54] as shown in figure 2.4. A primary electron beam of 2keV and 10\( \mu \text{A} \) with a 1mm\(^2\) spot size was directed at the sample. A linear,
Figure 2.4 Configuration of the LEED optics as a retarding field analyser for AES.
negative potential \((V_r)\) difference ramp was applied between the earthed sample and grids G2 and G3 so that only electrons with sufficient energy were collected by the screen. The resulting spectrum of total number of electrons reaching the screen versus energy was then electronically doubly differentiated \((3)\). This was achieved by modulating the applied potential with a small (~1-10V) sinusoidal signal of frequency \(\omega\) (1250 Hz) and recording the collector current signal with the lock-in amplifier (PAR-128) at the second harmonic frequency, \(2\omega\) \([7]\). This gives the derivative of the electron energy distribution, and has the effect of flattening out the slowly varying background and enhancing the small peaks caused by Auger electron emission.

2.4 Experimental LEED

2.4.1 LEED Optics and Electron Gun

Figure 2.5 is a schematic diagram of the 4-grid LEED optics and electron gun (Varian 951-2125) used in this work. Electrons emitted from a heated filament are collimated by the electrostatic lens and they leave the drift tube with an energy determined by the potential difference between the filament and the earthed sample. The drift tube is also earthed so as to provide a field free space for the electron beam. Typical beam energies used were 50-250eV with a current which varied linearly between \(\sim 0.1\mu A\) at 40eV and \(\sim 1\mu A\) at 100eV, and was constant at higher energies. This beam current as a function of energy was recorded following each measurement in order to normalise the LEED spot intensities.

The diffraction pattern is formed by the electron beams on the fluorescent screen after passage through the four concentric hemispherical grids labelled G1 to G4 in figure 2.5. Grid G1 is grounded so that backscattered electrons traverse a field free
Figure 2.5 Simplified diagram of the LEED optics used for displaying diffraction patterns.
space from the sample to G1. Grids G2 and G3 are at a negative potential, a few eV or so less than the incident electron energy to suppress inelastic electrons. Grid G4 is earthed in order to shield the suppressor grids from the high voltage of the collector screen (~5kV). This high potential accelerates the elastically scattered electrons from G4 onto the screen.

2.4.2 LEED Spot Intensity Measurements

The LEED spot intensities were measured as a function of incident electron beam energy using a vidicon TV camera (Coho 4410 ISIT) and a video LEED analyzer (VLA) from Data-Quire [55]. The set up is shown schematically in figure 2.6. The vidicon camera sends an image of the whole LEED screen to a monitor and to the microprocessor (MC6800) via an analogue to digital (A/D) convertor. The microprocessor also controls the LEED gun via a digital to analogue (D/A) convertor. The image of the LEED pattern on the monitor defines a video frame consisting of 256x256 pixels whose intensities can vary between 0 and 255. A diffraction spot is covered by a 10x10 pixel 'window' under computer control and its intensity is obtained by adding the intensities of the pixels in the window. The computer controls the movement of the window during data acquisition so that it tracks the path of the diffraction spot as the energy is increased. The VLA is capable of recording up to 49 spots simultaneously, but since some beams, especially the fractional beams, have very much smaller maximum intensities than other beams, which combined with the problem of obtaining adequate tracking for each spot, make it advisable to record different beam types separately, with different camera gain levels, in order to minimize background effects. The I(E) curves are then normalized according to the expression
Figure 2.6 Block diagram of the video LEED analyser (VLA).
\[ I = I'/I_0 \]

where \( I' \) and \( I_0 \) are measured diffracted and incident beam currents respectively. When a surface under investigation has point symmetry elements, and the direction of the incident beam is appropriately chosen, the diffraction pattern may contain symmetrically related spots. The procedure used is to average the \( I(E) \) curves measured for the symmetrically related beams; this helps to improve the spectra by averaging out slight inhomogeneities [56] and reducing the noise, as shown in figure 2.7. Such curves are then smoothed twice using a cubic spline routine, and if required, a background subtraction is made. The VLA used in this work had the option of inserting a delay between each measurement. The purpose of this delay is to ensure that the diffraction spot has stopped moving when its intensity is recorded. For a one second delay, this causes the surface to be under the electron beam for about ten times as long as when no delay is used. This increase in length of exposure to the electron beam is not a problem when the surface is stable under it, but for Cu(110)-(2x1)-O, the diffraction pattern was degraded quite quickly when the electron beam energy was above 200V.

### 2.4.3 LEED Spot Profile Measurements

Additional information regarding surface order can be obtained by measuring the intensity distribution across a given diffraction spot. The growth of chemisorption layers on a surface, for example, will inevitably be initiated at many places on a surface, which may lead to the formation of antiphase domains [27,57]. If the size of these domains is less than the transfer width of the instrument [33], then the observed diffraction pattern will have spots whose intensity distribution contains information on the domain structure, as well as step distribution, chemisorbed island sizes etc. Spot
Figure 2.7  I(E) curves for three symmetrically related beams from Cu(110)-(2x1)-O and two from Cu(311). These equivalent beams are averaged, smoothed, and if needed, the background is subtracted.
profile measurements are achieved with the VLA by placing a 10x10 pixel window completely over the spot to be analysed as shown in figure 2.8a. Ten scans are needed to digitize the spot (figure 2.8b). The intensity profile along the X_{win} direction is then obtained by joining the maxima of the ten profiles. The full width at half maximum (FWHM) of this spot profile gives a quantitative measure of spot sharpness [55]. In this work, the RFA was not sensitive enough to record Auger spectra of oxygen on the Cu(110) surface. Spot profile analysis of fractional beams from the Cu(110)-(2x1)-O system was thus essential to determine the optimum oxygen exposure required to give the best diffraction pattern.
Figure 2.8 LEED spot profile analysis:  a) a user selected 10x10 pixel window is placed over the diffraction spot  b) a LEED spot profile; the FWHM gives a measure of spot sharpness.
Chapter 3

Studies on the Copper (311) Surface
3.1 Introduction

The conceptual simplicity of low Miller index surfaces has resulted in a great deal of research conducted on them. The reactivity of 'real' surfaces however is thought to arise largely from the defect structures of the wide variety of crystal faces they exhibit. On high Miller index surfaces, the steps and kinks provide reproducible defects whose characteristics are fixed for a given surface. They have become important theoretically and experimentally as models to bridge the gap between the relatively well understood behaviour of low Miller index surfaces and the poorly understood surfaces of real polycrystalline materials.

The face centered cubic (311) surface is one of the simplest high Miller index surfaces, with a well defined step and terrace structure. Figure 3.1 gives the ideal bulk truncation, together with its corresponding reciprocal net (i.e. LEED pattern). It has the cm two dimensional space group, and can thus be represented by a centered rectangular net [24]. This surface is composed of steps with (100) and (111) components, as can be deduced from its alternative designations with the step and microfacet notations: 2(111)x(100) or 2(100)x(111) and 2t(100)+l1(111) respectively. The diperiodicity of this surface may also be represented by an oblique primitive net, whose unit mesh is sufficiently small to make it convenient for a multiple scattering LEED analysis.

The clean copper (311) surface has been studied previously in this laboratory [58,59,60]. In that study, a relaxation of the first interlayer spacing was the only structural parameter allowed to vary in matching experimental and calculated I(E) curves. The resulting contraction of -5.0±1.5% from the bulk interlayer spacing was well below that predicted by theory [61] and the result was also anomalous when compared to other f.c.c.(311) surfaces [62]. The relatively open (311) and (110) surfaces of Al and Ni as well as the (110) faces of other f.c.c. metals, have been shown
Figure 3.1  

a) The real space ideal bulk truncation representation of f.c.c.(311)

\begin{align*}
& (2,-4) (2,-3) (2,-2) (2,-1) (2,0) (2,1) (2,2) \\
& (1,-3) (1,-2) (1,-1) (1,0) (1,1) (1,2) (1,3) \\
& (0,-3) (0,-2) (0,-1) (0,0) (0,1) (0,2) (0,3) \\
& (-1,-2) (-1,-1) (-1,0) (-1,1) (-1,2) (-1,3) (-1,4) \\
& (-2,-2) (-2,-1) (-2,0) (-2,1) (-2,2) (-2,3) (-2,4)
\end{align*}

b) The reciprocal space f.c.c.(311) net (LEED pattern).
by LEED [63-66] and other techniques [67] to exhibit multilayer relaxations of the topmost interlayer spacings. These effects are more pronounced for more open surfaces. Recently a re-analysis of the original Cu(311) data, which consisted of 8 symmetrically inequivalent beams, using more sophisticated software which allowed consideration of these multilayer relaxations was performed [68]. The magnitudes of these damped oscillatory compressions and expansions, as given in table 3.1, were again considerably less than the values expected from theory [69,70] and in comparison to other f.c.c.(311) surfaces.

The original Cu(311) study was the first one performed in the Varian 240 vacuum chamber in this laboratory when the surface science group was still in its infancy, and was the first analysis of a high Miller index surface made anywhere using the dynamical theory of LEED. As well as testing theories for clean surfaces, another reason for undertaking new work on the Cu(311) surface is to attempt structural investigations when it contains adsorbates. No quantitative information exists for structural arrangements formed by chemisorption on stepped surfaces. These factors provided the impetus for a thorough re-investigation of the system.

3.2 Experimental Work on the Clean Copper (311) Surface

The copper (311) sample used in this work was prepared in the manner described in sections 2.1 and 2.2. Initial Auger spectra (figure 3.2a) indicated the presence of sulphur, chlorine and carbon. There could also have been substantial amounts of oxygen present, but the insensitivity to adsorbed oxygen of the LEED optics used as the Auger electron analyser, in common with other RFA's [53,71], meant that it could not be detected on a semi-quantitative level. As the Cu(311) surface became progressively cleaner, LEED patterns with streaks corresponding to partial
<table>
<thead>
<tr>
<th>Surface</th>
<th>d_B(Å)</th>
<th>d₁%</th>
<th>d₂%</th>
<th>d₃%</th>
<th>R-factor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(311)</td>
<td>1.22</td>
<td>-13.3</td>
<td>+8.8</td>
<td>0.0</td>
<td>R2,RZJ</td>
<td>66</td>
</tr>
<tr>
<td>Cu(311)</td>
<td>1.09</td>
<td>-5</td>
<td></td>
<td></td>
<td>RZJ</td>
<td>58</td>
</tr>
<tr>
<td>Cu(311)</td>
<td>1.09</td>
<td>-7.3</td>
<td>+3.7</td>
<td>0.0</td>
<td>R2,RPE,RZJ</td>
<td>68</td>
</tr>
<tr>
<td>Ni(311)</td>
<td>1.06</td>
<td>-15.9</td>
<td>+4.1</td>
<td>-1.6</td>
<td>R2</td>
<td>65</td>
</tr>
<tr>
<td>Theory</td>
<td>-12.2</td>
<td>+4.4</td>
<td></td>
<td>-1.7</td>
<td></td>
<td>69,70</td>
</tr>
</tbody>
</table>
Figure 3.2 Auger spectra of the Cu(311) surface.

a) Prior to cleaning in UHV.

b) After cleaning in by argon ion bombardment/anneal cycles.
ordering along the steps were observed, as had been reported previously [60]. This observation led to the sulphur adsorption experiments of section 3.3. After repeated bombard/anneal cycles, the concentrations of all surface contaminants were reduced to below the detection limit of the RFA as shown in figure 3.2b.

Intensity versus energy curves were recorded with a one second delay between each measurement for 14 beams including eight equivalent pairs at normal incidence for two separate experiments and a set of six I(E) curves, including three equivalent pairs, were taken at 10° off normal along the [233] azimuth so as to preserve the mirror plane in the LEED pattern. Table 3.2 gives the energy ranges over which LEED spot intensities were recorded for the Cu(311) surface, and the I(E) curves are shown in figures 3.3a-3.3t.

3.3 Adsorption of Sulphur on Cu(311)

3.3.1 Introduction

The adsorption of sulphur on the low Miller index faces of copper has attracted a great deal of attention from LEED crystallographers, and surface scientists in general [72,73]. In contrast, there have been few such studies of adsorption on the high Miller index surfaces of any metal [74]. The importance of such studies however, is evident from the role that sulphur is known to play in heterogeneous catalysis as a poison and as a catalyst pre-treatment agent [1]. A discussion of the experimental and theoretical difficulties of adsorption on stepped surfaces will be left until section 3.4.
Table 3.2 Beam indices and energy ranges (eV) for the experimental Cu(311) LEED I(E) curves.

<table>
<thead>
<tr>
<th>Beam Indices</th>
<th>Normal 1</th>
<th>Normal 2</th>
<th>Off-normal</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,-3),(-1,-2)</td>
<td>120 - 248</td>
<td>120 - 248</td>
<td>74 - 248</td>
</tr>
<tr>
<td>(1,-2),(-1,-1)</td>
<td>66 - 248</td>
<td>62 - 248</td>
<td>50 - 218</td>
</tr>
<tr>
<td>(1,-1),(-1,0)</td>
<td>50 - 248</td>
<td>50 - 248</td>
<td></td>
</tr>
<tr>
<td>(1,0),(-1,1)</td>
<td>50 - 248</td>
<td>80 - 248</td>
<td>50 - 248</td>
</tr>
<tr>
<td>(1,1),(-1,2)</td>
<td>50 - 248</td>
<td>80 - 248</td>
<td></td>
</tr>
<tr>
<td>(1,2),(-1,3)</td>
<td>120 - 248</td>
<td>120 - 248</td>
<td></td>
</tr>
<tr>
<td>(0,-3)</td>
<td>140 - 246</td>
<td>180 - 246</td>
<td>60 - 246</td>
</tr>
<tr>
<td>(0,-2)</td>
<td>110 - 246</td>
<td>104 - 226</td>
<td></td>
</tr>
<tr>
<td>(0,-1)</td>
<td>50 - 246</td>
<td>50 - 246</td>
<td></td>
</tr>
<tr>
<td>(0,2)</td>
<td>50 - 246</td>
<td>50 - 246</td>
<td></td>
</tr>
<tr>
<td>(0,1)</td>
<td>50 - 116</td>
<td>50 - 116</td>
<td>50 - 246</td>
</tr>
<tr>
<td>(0,3)</td>
<td>100 - 246</td>
<td>100 - 246</td>
<td></td>
</tr>
<tr>
<td>(2,-2),(-2,0)</td>
<td>150 - 248</td>
<td>192 - 248</td>
<td></td>
</tr>
<tr>
<td>(2,-1),(-2,1)</td>
<td>140 - 212</td>
<td>140 - 248</td>
<td></td>
</tr>
<tr>
<td>(0,0)</td>
<td></td>
<td></td>
<td>90 - 246</td>
</tr>
</tbody>
</table>
Figure 3.3 Experimental I(E) curves recorded for the clean Cu(311) surface.
Figure 3.3 cont. Cu(311) experimental I(E) curves.
Figure 3.3 cont. Cu(311) experimental I(E) curves.
Figure 3.3 cont. Cu(311) experimental I(E) curves.
Figure 3.3 cont. Cu(311) experimental I(E) curves.
Figure 3.3 cont. Cu(311) experimental I(E) curves.
o) (1,-3) and (-1,-2) beams at 10° off normal incidence.

p) (1,-2) and (-1,-1) beams at 10° off normal incidence.

q) (1,0) and (-1,1) beams at 10° off normal incidence.

Figure 3.3 cont. Cu(311) experimental I(E) curves.
Figure 3.3 cont. Cu(311) experimental I(E) curves.

r) (0,-3) beam at 10° off normal incidence.

s) (0,2) beam at 10° off normal incidence.

t) (0,0) beam at 10° off normal incidence.
3.3.2 Experimental

The streaked diffraction patterns caused by segregation of sulphur from the bulk copper could not be improved appreciably by longer or higher temperature annealing. This was reflected in the sulphur AES peak at 152eV, which did not increase in height for anneals of more than 10-15 minutes. To investigate whether adsorption of sulphur on the Cu(311) surface would produce a LEED pattern that was analyzable, a series of experiments whereby sulphur was adsorbed onto the Cu(311) surface by dosing with \( \text{H}_2\text{S} \), followed by heating to give the presumed desorption of \( \text{H}_2 \) were conducted. In this manner, the exposure conditions were optimized such that a LEED pattern which appeared to consist of \((2\times3)\text{S}\) and \((2\times5)\text{S}\) components was observed.

The clean Cu(311) surface was exposed at room temperature to high purity \( \text{H}_2\text{S} \) (Matheson Research Grade) at \( 2\times10^{-8} \) torr. During dosing, the previously sharp \((1\times1)\) LEED pattern was observed to degrade considerably. The integral spots became more diffuse with streaks joining them in the \([233]\) direction and halfway between the integral beams, also in the \([233]\) direction. Annealing of this surface for a few minutes at 300°C considerably reduced the background and partially ordered the streaks to form an ill-defined diffraction pattern.

To find the optimum \( \text{H}_2\text{S} \) dose, the LEED pattern was observed after annealing for a series of exposures, and sulphur uptake curves, measured by

\[
R = \frac{A_{152}}{A_{920}}
\]

i.e. the ratio of the AES peak-to-peak height for S at 152eV to that of Cu at 920eV, as a function of exposure were plotted (figure 3.4). The Cu peak at 920eV was chosen as it corresponds to a relatively deep core hole and so it is less sensitive to the presence of
Figure 3.4  Auger peak height ratio $R = \frac{S(152\text{eV})}{Cu(920\text{eV})}$ plotted as a function of $H_2S$ exposure time at $2 \times 10^{-8}$ torr.
adsorbed overlayers. The best diffraction patterns were observed for values of $R$ between about 2.5 and 3, which corresponded to an exposure of 3-4 minutes at $2 \times 10^{-8}$ torr $\text{H}_2\text{S}$. With higher exposures the pattern became very diffuse and no new LEED patterns were observed after annealing. In all cases, the patterns produced by dosing with $\text{H}_2\text{S}$ were superior to those caused by sulphur segregation from the bulk. This was presumably due to the higher surface concentration, as revealed by AES, of sulphur obtained on dosing.

3.3.3 Interpretation of the LEED pattern for sulphur on Cu(311)

Photographs of the LEED patterns obtained after dosing with $\text{H}_2\text{S}$ and annealing at 300°C are shown in figure 3.5a-3.5d. New spots in the LEED pattern were observed in the $[\bar{2}33]$ direction, both along the rows of integral spots and also halfway between these rows. The sharpest of these new spots were at $1/3$ and $2/3$ of the distance between integral spots, and so would be labelled $(h,k)$ where $h$ is an integer and $k = \{..., -5/3, -4/3, -2/3, -1/3, 1/3, 2/3, ...\}$. This implied the presence on the surface of regions of $(2\times3)$ translational symmetry. At certain energies however, still more spots were seen in the rows of $[\bar{2}33]$ direction, for example, at 62eV there were spots on either side of the $(1, -5/3)$ spot which can not be interpreted as being $(2\times3)$, but whose separation and position were consistent with a $(2\times5)$ pattern. Between rows of integral spots, the new diffraction spots were diffuse and tended to form streaks. At 62eV and 67eV however, pairs of spots could be seen whose separation was about a fifth of the integral beam separation, again consistent with a $(2\times5)$ diffraction pattern. From these observations it is reasonable to suggest that the observed pattern contained components from $(2\times3), (2\times5)$ and also $(2\times1)$ ordered regions of the surface (any fractional order spots from $(2\times1)$ regions would be in the same positions as those caused by diffraction
Figure 3.5 Photographs of the LEED pattern for sulphur adsorbed on Cu(311).
Figure 3.5 cont. Photographs of the Cu(311) - sulphur system.

c) 76eV

d) 142eV
off (2x3) and (2x5) regions). Moore [60] reported a similar combination of diffraction patterns on Ni(311) for sulphur that had diffused from the bulk to the surface during annealing. The occurrence of these composite patterns is perhaps not surprising when one examines the f.c.c.(311) surface and speculates on where adsorption could occur. It is clear that sulphur adsorbs along the terraces at every second site (as is observed for sulphur on the Cu(100) surface where it occupies the fourfold coordinate site to give a (2x2)S LEED pattern [73]), since the reported patterns all had a single row of fractional spots halfway between rows of integral spots in the [01\bar{1}] direction, though the actual site could not be ascertained from the diffraction pattern alone. The source of the streaks and the apparent superposition of diffraction patterns probably arises from the fact that for adsorbates on different rows, there are two symmetrically equivalent adsorption sites, as shown in figure 3.6a, which will lead to some randomness of adsorbate position between terraces. The actual situation though is rather more complex, as real f.c.c.(311) surfaces have many such terraces. This in turn would create LEED spots which are streaked along the [2\bar{3}3] direction. The general diffuseness of the diffraction spots is probably due to the size of the ordered regions. Since sites a and b in figure 3.6a are equivalent, long range order is unlikely, and therefore the dimension of ordering in the [\bar{2}33] azimuth will be less than the transfer width W. Figures 3.6b-3.6d show some plausible arrangements for sulphur adsorbed on Cu(311) which would give rise to (2x1), (2x3) and (2x5) diffraction patterns. I(E) curves were not recorded for this Cu(311)-sulphur system as the pattern was not of high enough quality for reliable data to be obtained, and for reasons to be discussed in the next section.
a) The two equivalent adsorption sites between adjacent terraces.

b) Possible arrangements of sulphur on Cu(311) which give (2x1) LEED patterns.

c) Possible (2x3) arrangements of sulphur on Cu(311).

d) Possible (2x5) arrangements of sulphur on Cu(311).

Figure 3.6 The adsorption of sulphur of the Cu(311) surface.
3.4 Some Considerations for Adsorption on Stepped Surfaces

In the layer doubling and RFS methods, diffraction matrices of the substrate and adsorbate layers can be calculated independently provided that the interlayer spacing between them is sufficiently large (>0.6Å and 1.0Å respectively). These matrices, representing diffraction from the layers may then be stacked to generate calculated diffraction beams from the whole surface region. The general openness of stepped surfaces however, leads to small interlayer spacings both for the substrate layers and the substrate-adsorbate layer. The former is a result of the angle at which the surface is cut with respect to the bulk unit cell vectors, and can be visualized from knowledge of the Miller indices, since these are proportional to the reciprocals of the points at which the crystallographic plane intercepts the unit cell vectors. Substrate-adatom layer spacings will tend to be small as the most favourable places for adatoms to stick will be in high coordination number sites adjacent to the steps (and kinks) on the surface.

The implication for multiple scattering analyses on stepped surfaces is that the topmost bulk layer and the adsorbate layer must often be treated as a single entity within the combined space approach. Often large unit meshes may be involved, but this would severely hinder the applicability of dynamical scattering calculations to such systems, given the computing resources at hand. The complexity of the calculations in all multiple scattering methods currently in use increases with the number of atoms in the unit mesh [5]. This means that study of adsorption on stepped surfaces will place great constraints upon researchers as regards computer time, cost and storage. Several schemes have been proposed that can reduce these requirements. The 'beam set neglect' (BSN) [75] and 'unit cell reduction' methods [76] consider only a small, carefully chosen subset of the diffracted beams during analysis. The BSN for example
improves the computation time by a factor of $N$ over the conventional generation and stacking of layer diffraction matrices, where $N$ is the number of atoms in the unit mesh. In Tensor LEED, by breaking down the scattering problem into a structure factor and a form factor, such that it becomes analogous to X-ray scattering [77], advantages in computer time over conventional methods have been shown to approach three orders of magnitude. In addition, efficient use of symmetry in both real and reciprocal spaces have recently enabled analysis by dynamical LEED of the Si(111)-(7x7) reconstructed surface [78]. As well as making an analysis more difficult, the actual acquisition of data becomes progressively harder as the unit mesh size increases. This is because the spacing between diffraction spots is inversely proportional to the geometrical size of the surface unit cell, and therefore emphasises the need for higher resolution instruments [79].

In view of the difficulties concerning quantitative LEED analysis for chemisorption on stepped surfaces, and the fact that it is an area as yet unexplored by dynamical LEED, any system to be studied at present should satisfy certain criteria. Firstly, preparation of the surface itself and adsorption of gases needs to be carried out very carefully so as to be sure that the observed diffraction pattern is genuinely sharp and not a composite of patterns from different arrangements of the same adsorbate, as was observed for sulphur on the Cu(311) surface. Secondly, the unit mesh of the substrate needs to be as small as possible (correspondingly the interlayer spacing should be as large as possible) in order that a perturbative dynamical method may be available for the LEED intensity calculations. Third, the unit mesh of the substrate-adsorbate system should be as small as possible since the number of beams required in a calculation (and hence the dimension of square matrices involved) increases in proportion to the unit mesh area [44]. Therefore the ideal systems for investigating
adsorption on stepped surfaces would show (1x1) or (2x1) diffraction patterns. Table 3.3 gives some characteristics of the seven simplest f.c.c. stepped surfaces that are pertinent to LEED crystallography.

With specific regard to stepped surfaces of copper, the Cu(210)-(2x1)-O pattern reported by McKee et. al. [84] seems eminently analyzable by dynamical LEED. This surface has long bridge sites that are not dissimilar to those found on the Cu(110) surface (see chapter 4). The f.c.c.(210) surface though, in common with other surfaces with oblique unit meshes, may suffer from the statistical randomness of adsorption site which was seen for Cu(311)-sulphur, leading to one-dimensional ordering. In that respect, stable and unique adsorbate arrangements are unlikely unless some form of surface reconstruction occurs or unless (1x1) structures are possible with the adsorbed species. With this in mind, perhaps the best f.c.c. stepped surfaces for LEED crystallographic analyses would be the (211), (221) and (310) faces, as these have rectangular unit meshes. The Cu(410)-(1x1)-O and Cu(410)-(1x1)-2O patterns reported by Milne [89], Algra et. al. [90] and Thompson et. al. [91], though apparently well-defined, would not be amenable to dynamical LEED analysis due to the small interlayer spacings. On high Miller index surfaces of body centered cubic (b.c.c.) and hexagonal close packed (h.c.p.) lattices, the same principles and suggestions made for f.c.c. surfaces should also apply. Tables 3.4a and 3.4b give some characteristics helpful to LEED crystallographers for the simplest b.c.c. and h.c.p. high Miller index surfaces respectively which possess rectangular unit meshes. It should be noted in the case of b.c.c. and h.c.p. crystal lattices however, that not all high Miller index surfaces are in fact stepped. Also some h.c.p. surfaces are not unique, such that for a given Miller index, there may be two possible surface structures as a result of the 'non-unique plane' problem. This in turn would further complicate a calculational analysis so the best h.c.p. surface to study would probably be the (110) surface. Although this
Table 3.3  Characteristics of the seven simplest f.c.c. stepped surfaces.

<table>
<thead>
<tr>
<th>Unit mesh</th>
<th>Notation</th>
<th>Dimensions</th>
<th>Known simple adsorption systems</th>
<th>Refs.</th>
</tr>
</thead>
</table>
| ![Image](image1) | 311 2(100)x(111) 1_{1}(100)+1_{1}(111) | a = r  
  b = \sqrt{3}r  
  \theta = 106.78^\circ  
  A = 1.66r^2  
  d = 0.426r | Au: (5x3)Pb, (3x3)Pb  
  Cu: (4x2)Pb  
  Ni: (2x1)S, (2x3)S,(2x5)S  
  Pd: (2x1)CO | [80] |
| ![Image](image2) | 210 2(100)x(110) 1_{1}(100)+1_{1}(110) | a = \sqrt{2}r  
  b = \sqrt{3}r  
  \theta = 114.09^\circ  
  A = 2r^2  
  d = 0.316r | Au: (1x1)Pb  
  Cu: (2x1)O, (3x1)O, (2x3)N  
  c(11\sqrt{2}x\sqrt{2})R45^\circ N  
  Ni: c(11\sqrt{2}x\sqrt{2})R45^\circ N, (2x3)N  
  Pd: (1x1)CO, (1x2)CO | [83] [84] [85] |
| ![Image](image3) | 331 3(111)x(100) 1_{2}(111)+1_{1}(100) | a = r  
  b = \sqrt{5}r  
  \theta = 102.92^\circ  
  A = 2r^2  
  d = 0.324r | Ag: (6x1)Cl  
  Rh: (1x1)H_2 | [87] |
| ![Image](image4) | 211 3(111)x(100) 1_{2}(111)+1_{1}(100) | a = r  
  b = \sqrt{6}r  
  \theta = 90^\circ  
  A = 6r^2  
  d = 0.289r | Cu: (4x1)Pb | [81] |
| ![Image](image5) | 221 4(111)x(111) (3/2)_1(111)+1_{1}(111) | a = r  
  b = 3r  
  \theta = 90^\circ  
  A = 3r^2  
  d = 0.236r | | |
| ![Image](image6) | 310 4(100)x(110) 3_{1}(100)+1_{1}(110) | a = \sqrt{2}r  
  b = \sqrt{5}r  
  \theta = 90^\circ  
  A = 10r^2  
  d = 0.224r | | |
| ![Image](image7) | 410 4(100)x(110) 3_{3}(100)+1_{1}(110) | a = \sqrt{2}r  
  b = (\sqrt{17}/2)r  
  \theta = 104.04^\circ  
  A = 4r^2  
  d = 0.171r | Cu: (1x1)O, (1x1)2O | [89] [90] [91] |
Table 3.4a  Some characteristics of the three simplest b.c.c. high Miller index surfaces with rectangular unit meshes.

<table>
<thead>
<tr>
<th>Unit mesh</th>
<th>Notation</th>
<th>Dimensions</th>
</tr>
</thead>
</table>
| ![Diagram](image1.png) | 211  
2(111)x(100)  
1₁(111)+₁₁(100) | $a = r$  
b = $(\sqrt[8]{3})r$  
$A = (\sqrt[6]{8})r^2$  
d = $(\sqrt[2]{18})r$ |
| ![Diagram](image2.png) | 210  
2(110)x(100)  
1₂(110)+₁₁(100) | $a = (\sqrt[2]{3})r$  
b = 2.581$r$  
$A = 2.981r^2$  
d = 0.258$r$ |
| ![Diagram](image3.png) | 332  
3(111)x(110)  
2₂(111)+₁₂(110) | $a = (\sqrt[8]{3})r$  
b = $(\sqrt[8]{132})r$  
$A = 3.127r^2$  
d = 0.246$r$ |
Table 3.4b  Some characteristics of the four simplest non-basal h.c.p. surfaces with rectangular unit meshes.

<table>
<thead>
<tr>
<th>Unit mesh</th>
<th>Notation</th>
<th>Dimensions</th>
</tr>
</thead>
</table>
| ![Diagram](image1) | 100 1010 | a = r  
b = \((\sqrt{8}/\sqrt{3})r\)  
A = \((\sqrt{8}/\sqrt{3})r^2\)  
d = \(1/3(\sqrt{3}/2)r\) or \(2/3(\sqrt{3}/2)\) |
| ![Diagram](image2) | 102 1012 | a = r  
b = \((\sqrt{51}/\sqrt{3})r\)  
A = \((\sqrt{51}/\sqrt{3})r^2\)  
d = 0.198r or 0.396r |
| ![Diagram](image3) | 110 1120 | a = \((\sqrt{8}/\sqrt{3})r\)  
b = \(\sqrt{3}r\)  
A = \(\sqrt{8}r^2\)  
d = 0.5r |
| ![Diagram](image4) | 112 1122 | a = \(\sqrt{3}r\)  
b = \((\sqrt{22}/\sqrt{6})r\)  
A = \((\sqrt{44}/2)r^2\)  
d = 0.426r |

In this table \(\delta\) is a number such that 0\(\leq\delta<1\). This \(\delta\) specifies the location of the dividing plane (i.e. bulk termination), leading to non-unique surfaces for a given (hkl) plane when (2h+4k+3l) is not a multiple of six. The notations given here are Miller indices and Miller-Bravais indices, a four index system given by (hk-(h+k)l). The step notation has not been given here since for h.c.p. surfaces it does not give a convenient description of the surface. Also, the microfacet notation is only applicable to cubic lattices.
surface is not strictly stepped or even of high Miller index in the normal sense of the term, it does contain regular 'defects' which stem from its relatively open nature, and therefore study of its surface properties would be helpful as a precursor to the study of h.c.p. high Miller index surfaces proper. It remains to be seen whether the study of adsorption systems on high Miller index surfaces using LEED will have a comparable degree of success to studies on the low Miller index surfaces.
Chapter 4

Studies on the Copper (110)-\((2\times1)\)-O Adsorption System
4.1 Introduction and Previous Work

The adsorption of oxygen on metallic surfaces is of considerable interest in heterogeneous catalysis research [1]. For more than two decades, the interaction of oxygen with the low Miller index surfaces of copper has occupied many surface scientists, resulting in a great deal of work using various surface sensitive techniques.

From the earliest LEED studies [92], it has been known that oxygen adsorption at room temperature leads to the formation of a stable (2x1) superstructure on Cu(110) which corresponds to a half monolayer coverage. Upon further exposure to O₂, this is replaced by a c(6x2) structure, and then a surface oxide layer of Cu₂O is observed to form [92]. Figure 4.1 shows the Cu(110) surface along with its LEED patterns before and after oxygen exposure up to the half monolayer coverage. The aforementioned studies have provided much information regarding adsorption site, which is now universally accepted as the long bridge site in the [001] direction, as well as conflicting evidence regarding the occurrence and nature of reconstruction in the substrate, interlayer spacings and bond lengths. For confirmation of a proposed surface structure model, modern surface science requires that there be agreement between results from different surface analytical tools. The controversy surrounding the structure of the Cu(110)-(2x1)-O adsorption system stems from discrepancies that exist in analyses using a variety of surface structure probes. Table 4.1 summarises the structural information obtained for this system to date. Techniques used thus far include three types of ion scattering spectroscopies namely ICISS [93], LEIS [94] and HEIS [95] as well as atom diffraction [96], SEXAFS [97,99], NEXAFS [98], angular resolved UPS [100] and GIXS [101]. The surface structure models proposed so far are presented in figure 4.2a-d. The problem of attempting to compare the results from these different techniques is due to two main factors. Firstly, each is sensitive to different features of
Figure 4.1  a) A real space ideal bulk truncation representation of the f.c.c.(110) surface.

b) The reciprocal space f.c.c.(110) net (LEED pattern).

c) LEED pattern of the Cu(110)-(2x1)-O adsorption system.
<table>
<thead>
<tr>
<th>Technique</th>
<th>Adsorption site</th>
<th>Model</th>
<th>$d_{\text{Cu-O}}$</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$\theta$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICISS</td>
<td>long bridge</td>
<td>missing row</td>
<td>$+25%$</td>
<td>$-10%$</td>
<td>$\pm10%$</td>
<td>$\pm5%$</td>
<td>0.5ML [93]</td>
</tr>
<tr>
<td>LEIS</td>
<td>long bridge</td>
<td>missing row</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5ML [94]</td>
</tr>
<tr>
<td>HEIS</td>
<td>long bridge</td>
<td>buckled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5ML [95]</td>
</tr>
<tr>
<td>HEAD</td>
<td>long bridge</td>
<td>missing row</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\leq0.5$ML [96]</td>
</tr>
<tr>
<td>SEXAFS</td>
<td>long bridge</td>
<td>missing row</td>
<td>$+0.35\AA$</td>
<td></td>
<td></td>
<td></td>
<td>0.5ML [97,99]</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>long bridge</td>
<td></td>
<td>$+0.35\AA$</td>
<td></td>
<td></td>
<td></td>
<td>0.5ML [98]</td>
</tr>
<tr>
<td>ARUPS</td>
<td>long bridge</td>
<td>buckled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5ML [100]</td>
</tr>
<tr>
<td>GIXS</td>
<td>long bridge</td>
<td>buckled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5ML [101]</td>
</tr>
</tbody>
</table>
Figure 4.2  Proposed models for the Cu(110)-(2x1)-O surface.
the surface such as long and short range order, and also, the conditions under which the surfaces were prepared and analysed were not always the same. For example, the HEIS study, favoured a buckled row model whereas LEIS and ICISS suggested a missing row model. Due to the high sputtering yields for Cu and O using 4keV Ne\(^+\) ions, the LEIS work was carried out under conditions of dynamic equilibrium, and therefore one cannot rule out the existence of a different surface structure to that studied by other techniques and HEIS, where the sputtering yields are less as a result of the smaller cross section for sputtering by 500keV He\(^+\) ions. The LEIS study concluded that oxygen sits 0.6±0.2Å below the top Cu layer and ICISS, using 5keV Li\(^+\) ions, gave values for the top two Cu interlayer spacings of +25±10% and -10±5% from the bulk Cu(110) interlayer spacing. Atom diffraction does not suffer from the same problem of experimentally induced surface damage. In particular, helium atoms with <0.1eV energy do not penetrate the topmost copper layer, and so structural information from HEAD should be more reliable. For clean Cu(110) it was found that helium atoms are relatively insensitive to the corrugation of the surface, yielding a value of 0.09Å for the depth of the troughs. This is due to a 'smoothing out' of the Cu ion cores by valence electrons so that the He atoms could not 'see' much of the corrugation of the surface. After adsorption of half a monolayer of oxygen however, a corrugation depth of 0.75Å was obtained. This along with analysis of the diffraction peaks, provided evidence for a 'missing row' structure, but no quantitative values for interlayer spacings or Cu-O bond lengths were given. In the angle resolved UPS and GIXS work, the buckled surface model explained the experimental findings better than other models, but again, no values were given for interlayer spacings or for the heights of the proposed 'buckles'.
Techniques such as SEXAFS and NEXAFS are sensitive to short range order, but give less information regarding interlayer spacings or relaxation phenomena. In the SEXAFS work, the buckled row model was rejected purely on nearest neighbour bond length determinations since a peak corresponding to the distance between oxygen and copper atoms in the buckled row were missing. NEXAFS also favoured the missing row model using a similar premiss and gave good agreement with SEXAFS for the height of oxygen above the copper atoms that they bridge of +0.35 Å, a rather different value to that obtained by LEIS of -0.6±0.2 Å. To date, no quantitative surface structure analysis by LEED has been published for the system using full dynamical scattering calculations of I(E) curves. This chapter presents experimental data obtained for nine symmetrically inequivalent beam types recorded at normal incidence and six at 10° off-normal for the Cu(110)-(2x1)-O system.

4.2 Experimental

The Cu(110) sample was prepared in the same way as the Cu(311) sample, as described in sections 2.1 and 2.2. Prior to cleaning in UHV, the surface was found to be contaminated with sulphur, carbon and chlorine. Since both the Cu(311) and Cu(110) samples were cut from the same single crystal rod, and the preparation procedures were essentially identical, it is not surprising that both contained the same amount and type of contaminants. After cleaning in UHV by argon ion bombardment, it was necessary to find the oxygen exposure which produced the best (2x1) diffraction pattern. This was achieved by dosing with varying amounts of oxygen, followed by annealing at 100°C for five minutes. Spot profiles were then recorded for the (1,-1/2) and (-1,-1/2) fractional beams and plotted (see figure 4.3). This allowed accurate determination of the optimum exposure conditions. During data acquisition, the LEED
Figure 4.3 Normalised 1/FWHM of the (1,-1/2) and (-1,-1/2) fractional beams from the Cu(110)-(2x1)-O surface plotted as a function of exposure time to oxygen at 4x10⁻⁸ torr.
pattern was observed to degrade slowly under the electron beam, resulting in increased background and diffuse diffraction spots. For this reason, the sample was re-annealed after every third set of beam intensity measurements. Intensity versus energy curves were recorded for five fractional and four integral order beams at normal incidence in two separate experiments, and two sets of data for six integral order beams were recorded at 10° off normal incidence along the [110] azimuth. The surface was then re-positioned normal to the electron beam, and the original nine beams were re-recorded twice to check their correspondence to the first two sets of normal data.

4.3 Presentation of Data

The energy ranges over which each beam was recorded are given in table 4.2, and their I(E) curves are shown in figures 4.4a to 4.4o. In the first two sets of normal data and the off-normal data, a one second delay was inserted between each intensity measurement. This resulted in a visible degradation of the diffraction pattern after recording of three different beam types due to the length of exposure to the electron beam. The third and fourth sets of normal data were recorded without a delay, so as to minimize the time that the surface was under the electron beam in each scan. This also allowed multiple scans to be added, with corresponding increase in the signal to noise ratio. After recording three inequivalent beam types, the total time that the electron beam was on, was about the same as that for data collected with a delay. Comparison of peak positions in I(E) curves recorded by these two methods reveals a systematic shift to lower energy by about 4eV for curves recorded without a delay. The shift can be attributed to the spot intensities being recorded a fraction of a second before the diffracted beams had stopped moving. In a multiple scattering calculation, this shift would be taken into account by variation of the inner potential V_{or}. Since this is a non-
Table 4.2 Beam indices and energy ranges (eV) for the experimental Cu(110)-(2x1)-O LEED I(E) curves.

<table>
<thead>
<tr>
<th>Beam Indices</th>
<th>Normal 1</th>
<th>Normal 2</th>
<th>Off normal 1</th>
<th>Off normal 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,1),(0,-1)</td>
<td>50-180</td>
<td>50-248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1,1),(-1,1),(1,-1),(-1,-1)</td>
<td>50-248</td>
<td>100-248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2,0),(-2,0)</td>
<td>100-230</td>
<td>50-248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2,1),(-2,1),(2,-1),(-2,-1)</td>
<td>104-248</td>
<td>100-248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1,1/2),(-1,1/2),(1,-1/2),(-1,-1/2)</td>
<td>50-248</td>
<td>50-248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2,1/2),(-2,1/2),(2,-1/2),(-2,-1/2)</td>
<td>104-248</td>
<td>80-248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,1/2),(0,-1/2)</td>
<td>50-130</td>
<td>50-148</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,3/2),(0,-3/2)</td>
<td>80-206</td>
<td>80-248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1,3/2),(-1,3/2),(1,-3/2),(-1,-3/2)</td>
<td>100-206</td>
<td>100-248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-1,1),(-1,-1)</td>
<td></td>
<td></td>
<td>50-218</td>
<td></td>
</tr>
<tr>
<td>(0,1),(0,-1)</td>
<td></td>
<td></td>
<td>50-218</td>
<td>50-218</td>
</tr>
<tr>
<td>(-1,0)</td>
<td></td>
<td></td>
<td>50-134</td>
<td>50-134</td>
</tr>
<tr>
<td>(-2,0)</td>
<td></td>
<td></td>
<td>50-134</td>
<td>50-134</td>
</tr>
<tr>
<td>(0,2),(0,-2)</td>
<td></td>
<td></td>
<td>80-218</td>
<td>80-218</td>
</tr>
<tr>
<td>(0,0)</td>
<td></td>
<td></td>
<td>100-198</td>
<td>100-198</td>
</tr>
</tbody>
</table>
Figure 4.4 Experimental I(E) curves recorded for the Cu(110)-(2x1)-O surface.
c) (2,0) and (-2,0) beams at normal incidence.

d) (2,1), (-2,1), (-2,-1) and (-2,-1) beams at normal incidence.

Figure 4.4 cont. Cu(110)-(2x1)-O experimental I(E) curves.
Figure 4.4 cont. Cu(110)-(2x1)-O experimental I(E) curves.
Figure 4.4 cont. Cu(110)-(2x1)-O experimental I(E) curves.
Figure 4.4 cont. Cu(110)-(2x1)-O experimental I(E) curves.

j) (-1,1) and (-1,-1) beams at 10° off normal incidence.

k) (0,1) and (0,-1) beams at 10° off normal incidence.
Figure 4.4 cont. Cu(110)-(2x1)-O experimental I(E) curves.
Figure 4.4 cont. Cu(110)-(2x1)-O experimental I(E) curves

n) (0,2) and (0,-2) beams at 10° off normal incidence.

o) (0,0) beam at 10° off normal incidence.
structural parameter, it would not alter the shape of the calculated I(E) curves, only their position on the energy scale during matching of experimental and theoretical I(E) curves would be affected.

4.4 Final Comments and Suggestions for Further Work

This thesis aims to add to our knowledge of copper surfaces, in particular the stepped Cu(311) surface and its interaction with sulphur and also oxygen adsorption on the Cu(110) surface. LEED and AES together are particularly suited to this task, the former providing detailed structural information, while the latter gives the elemental composition of the surface. It had been hoped to include a multiple scattering analysis for the Cu(311) surface using at least the normal incidence data. These calculations, as well as forthcoming calculations for the off-normal data, have been performed by Dr P.R. Watson at Oregon State University. Due to unforeseen circumstances however, the matching of experiment and theory using the R-factors R2, RZJ and RPe has not been completed as yet, though a full analysis using all the experimental data is imminent.

The work on sulphur adsorption on Cu(311), though inconclusive in that it was not able to unambiguously determine the nature of sulphur atom ordering on the surface, did highlight the many problems associated with chemisorption on stepped surfaces. The conclusions drawn and suggestions made will benefit those attempting LEED crystallography on such systems in the future. In addition, a full multiple scattering analysis of the Cu(110)-(2x1)-O chemisorption system is currently being initiated in the surface science laboratory at UBC.

More detailed investigations into surface phenomena, over and above surface structural analyses are also needed. The use of optical transform methods [102] for
modelling complex diffraction patterns should become more widespread in the future, in principle this relatively simple process could allow unambiguous determination of LEED patterns. Techniques such as HREELS can give detailed information regarding surface vibrations, thermal desorption spectroscopy allows accurate determination of chemisorption energies, and other structure probes such as SEXAFS, ARXPS, ion scattering etc. should in principle allow unambiguous structure determination following the multi-technique approach to surface crystallography. Dynamic processes, including chemical reactions, are also now assuming increased importance in surface science.
References
References