Instabilities of Vicinal Silicon (111) Surfaces

by

Monte Jerome Ramstad

Submitted to the Department of Physics
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

February 1996

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Abstract

The morphological instabilities of vicinal Si(111) due to a DC electric current and
due to the 7 x 7 reconstruction are studied using a variety of diffraction and imaging
techniques. The current induced instabilities which occur at sublimation temper-
atures or under conditions of step-flow produce morphological features on length scales
appropriate for optical studies, 5 - 50μ. Optical microscopy, a laser diffraction tech-
nique atomic force microscopy (AFM) and high resolution x-ray diffraction have been
applied to these surfaces. In addition to the step bunching instabilities reported by
others, these techniques reveal a transverse instability in the step profiles for current
flowing in the step-down direction at all temperatures between 700° C and 1300°
C. For the same current direction, the step bunching instability is observed below
1025° ± 15° C and above 1230° ± 15° C up to at least 1300° C. On the other hand, for
current flowing in the step-up direction, the step profiles are stabilized and the step
bunching instability is observed between 1025° ± 15° C and 1230° ± 15°. Stoyanov’s
theory of the current driven step-bunching instabilities is reviewed and extended to
explain the step wandering instabilities by modifying the boundary conditions of a
diffusion equation at the step edges. Measurements of the rate of growth of the
transverse instability indicate an activation energy of 2.7 ± 0.1 eV.

Near the 7 x 7 reconstruction temperature, \( T_c = 870° \) C, a faceting transition
occurs. We have investigated the time and temperature dependence of the spinodal
decomposition of step bands and the approach to the equilibrium crystal shape. The
equilibrium shape profile exhibits critical behavior \( z \sim x^\alpha \) where \( \lambda = \alpha/(\alpha - 1) = 3.0 ± 0.1 \) which is consistent with a Pokrovsky-Talapov transition.

Thesis Supervisor: Robert J. Birgeneau
Title: Dean of Science and Cecil and Ida Green Professor of Physics
Acknowledgments

This work was made possible by the contributions of many people. First, I would like to thank my parents for their unwavering love and support which has helped me persevere in hard times. I would also like to thank Yoko and Laura and my son for making my years at MIT the most productive and enjoyable of my life.

The people who were involved in this work are Michael Young, Do-Young Noh, Barry Wells, Ken Blum and Bob Birgeneau. I am personally in debt to Michael Young and Barry Wells who contributed substantial amounts of time and effort to this project on my behalf. I would also like to thank the past and present students of professors Bob Birgeneau and Simon Mochrie, and the staff at Brookhaven National Laboratory and IBM, Yorktown who have built and maintained various equipment, laboratories, and computer facilities. They include Doug Abernathy, Rene Holaday, Jean Jordan-Sweet, Glenn Held, Brian Stephenson, Simon Mochrie, Bob Birgeneau, Michael Young, Alan Mak, Do-Young Noh, Barry Wells, John Hill, Tom Thurston, Bill Nuttall, Brian McClain, Bernhard Keimer, Alec Sandy, Gerry Swislow, Ken Evans-Lutterodt, Mirang Yoon, Seungheon Song, Qiang Feng, Joan Harris, Martin Greven, Young Lee, Young-June Kim, Yongmei Shao, and Kevin Fahey.

Over the course of my education, I have benefited from the exceptional character, generosity, and integrity of several professors and teachers which include Mr. Marty Cordes, Prof. Matthew Tirrell, Prof. Robert Brown and Prof. George Clark.
To my grandfather . . .
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Chapter 1

An Overview

1.1 Introduction

The behavior of surfaces in various environments has been a topic of great interest due to its importance to surface engineering. The manufacture of various types and arrays of electronic devices and films on crystal surfaces as well as the production of crystals themselves all depend on the properties and behavior of the crystal surface or interface. The desire to understand and control the behavior of surfaces has motivated a large amount of experimental and theoretical work. Vicinal surfaces (crystal surfaces oriented near to a high symmetry direction) are ideal systems for studying surface anisotropy.

The scope of this thesis is to report our investigations of the various instabilities of vicinal Si(111) which include phase separation due to the 7 x 7 reconstruction, step bunching due to a current effect, and transverse step instabilities which are also due to a current effect. This study is an extension of the earlier studies initiated by Do Young Noh[41, 42]. The initial scope of his study was to characterize the 7 x 7 reconstruction driven faceting transition which occurs near the reconstruction temperature $T_c = 870^\circ$ C and to characterize the fluctuations of the uniformly stepped phase. However, in the course of this study, a sublimation induced faceting (thermal faceting) instability was discovered above about 1025$^\circ$ C. This instability was recognized as one of a set of instabilities which depend on the direction of the DC current used to heat the
In this chapter, an overview of the instabilities on vicinal Si(111) is presented. A phase diagram is presented which provides a summary of the major results of this work. Next, the atomic structures of an un-reconstructed vicinal surface and a 7 × 7 reconstructed surface are described. The fact that the 7 × 7 reconstruction is a first order transition provides an experimental trick for measuring the equilibrium crystal shape. Therefore, the Wulff construction which provides a relationship between quasi-equilibrium vicinal surfaces and the equilibrium crystal shape is reviewed. Since measurements of the changing surface morphology form an integral part of this work, the non-equilibrium aspects of phase separation are also introduced. At sublimation temperatures, the surface behavior is governed by the stability of step-flow therefore, the fundamental equations of step flow are presented. These concepts provide the foundation for the more detailed theoretical results discussed in later chapters.

In chapter 2, the techniques of X-ray diffraction, laser diffraction, atomic force microscopy (AFM), and optical microscopy (OM) are discussed. In addition, the various developments in sample heating and temperature control which were needed for studies at sublimation temperatures are described. In chapter 3, the first experiments which mapped out the instabilities are discussed. A study of flashing indicates the preferred flashing conditions for cleaning the surface while producing a uniform step phase. In chapter 4, a model introduced by Stoyanov[50] to explain the current driven step bunching instabilities is reviewed. Extensions of this model are proposed to explain the step rippling instability. In chapter 5, optical microscopy and atomic force microscopy (AFM) images of the current induced instabilities 1025° C are presented and compared with model predictions. In chapter 6, a corresponding study using laser diffraction is presented. These in situ studies allow growth rates to be measured.

The second part of this thesis is devoted to the equilibrium crystal shape (ECS). A review of the theoretical results is given in chapter 7. In summary, the ECS of rough surfaces are predicted to have a mean-field critical exponent whereas the ECS of smooth surfaces are predicted to have a Pokrovsky-Talapov critical exponent.
Previous experimental measurements of the ECS on small crystals and vicinal surfaces is given in chapter 8. In chapters 9 and 10, the results of our x-ray measurements on vicinal Si(111) surfaces are presented. Chapter 9 deals with the non-equilibrium aspects of the faceting transition near the $7 \times 7$ reconstruction temperature while Chapter 10 deals with measurements of the ECS.

1.2 The Phase Diagram

A phase diagram of the instabilities on a vicinal Si(111) surface miscut $3^\circ$ toward the $< 11\bar{2} >$ direction is shown in figure 1.2. Here positive current is defined to flow toward the miscut direction or in the step-down direction. The step bunching instabilities are indicated by left hatching ($//)$ while the $7 \times 7$ reconstruction driven faceting transition is indicated by right hatching. One might note that the phase diagram in figure 1.2 does not include the time related aspects of the instabilities which are also quite important.

The effects of current direction are important over the full temperature range of these studies. The current direction of the step-bunching instability reverses polarity with increasing temperature at at least two inversions temperatures, $T_i$. On the other hand, the transverse instability occurs only for positive current at all temperatures. The borders of the instability regions are believed to be sharp however, the absolute and relative temperatures are not well known except for those associated with the $7 \times 7$ reconstruction. A similar set of the current effected faceting instabilities were first reported by Latyshev[34, 35] for a $8'$ miscut Si(111) surfaces whereas the transverse instabilities were first discovered during our studies using a laser diffraction.

The phenomena of crystal surface faceting is well understood and is well covered in the literature. In 1928, Gibbs[14] clarified the fundamental thermodynamic properties of surfaces which allow the surface to be described as a phase. In 1901, Wulff[57] demonstrated that the surface free energy is related to the macroscopic equilibrium crystal shape (ECS). Furthermore in 1951, Herring[19] stated several theorems associated with the faceting of vicinal surfaces. Based on this foundation, measurements
Figure 1-1: Phase Diagram of Vicinal Si(111)
on crystals and on vicinal surfaces at equilibrium can provide information concerning
the functional form of the free energy of vicinal surfaces. These experiments can be
compared with the predictions of several models of step interactions which have been
solved exactly.

In contrast, the thermal faceting due to the current effect is not well understood
and few theoretical explanations have been proposed. Stoyanov[50] has proposed
one theory which is based on an electromigration hypothesis. While this theory
can account for a current effected step bunching instability near a single inversion
temperature, it does not account for the observation of more than one inversion
temperature. In addition, no satisfactory explanation has been proposed for the
current effected transverse instabilities.

1.3 The Structure of Vicinal Si(111) Surfaces

In practice, highly ordered crystal surfaces are obtained by cleaving or by cutting
and polishing a bulk specimen. Cleaving can sometimes be used to produce surfaces
at discrete cusps in the surface free energy as a function of orientation. Cusps occur
at high symmetry orientations which have low Miller indices such as (111) or (100).
On the other hand, cutting and polishing is used to produce a surface in the cutting
plane which is selected from a continuum of orientations. This technique was used
by the commercial manufacturer, Virginia Semiconductor, Inc., which produced our
Si samples.

The lattice positions of the top bilayer of atoms of a perfectly truncated vicinal
Si(111) surface, which has a diamond lattice structure, is shown in figure 1.3. Surfaces
which are cut vicinal to a high symmetry orientation can be described as a set of
terraces with a high symmetry orientation separated by atomic steps with a particular
density. In figure 1.3, two atomic steps are shown separated by about 55Å or by about
the average step spacing for a 3.5° miscut. The (111) terraces between the steps have
three mirror symmetries through the < 11\(\bar{2}\) >, < 1\(\bar{2}\)1 >, and < 2\(\bar{1}\)1 > axes. However,
the miscut toward < 11\(\bar{2}\) > eliminates two of these symmetries leaving only the
Due to the ABCABC... stacking of the bilayers, the two steps in figure 1.3(a) separate A, B, and C bilayers as shown. Each neighboring bilayer is shifted by 1/3 of the lattice periodicity along the \( \langle 11\overline{2} \rangle \) direction. The open circles represent atoms on the top half of the first bilayer of each terrace while the small closed circles represent atoms on the bottom half of the first bilayer. The truncation as shown breaks one bond per atom on the top half of the bilayer on the (111) terraces and one bond per atom on the lower half of the bilayer along a step edge. Steps on vicinal surfaces miscut in the opposite direction (i.e. \( 3^\circ \rightarrow \langle \overline{1}1\overline{2} \rangle \)) have two broken bonds per atom on the lower half of the bilayer along a step edge. Therefore, different behavior may be expected on vicinal surfaces with opposite miscut directions.

On real surfaces, the atomic positions and electronic distributions relax near the surface in order to minimize the surface free energy. Due to the large density of broken bonds, the true structure of the surface near a step may be much different from the truncation shown in figure 1.3(a). However in this work, the exact structure of the steps is not of concern. Instead, the goal is to characterize the behavior of the steps which arises from general step interactions.

1.4 The Structure of the 7 × 7 Reconstruction

Structural transformations on the (111) terraces can cause an increase in the periodicity from that of a perfectly truncated surface. When the periodicity changes by integer factors \( N \) and \( M \), the resultant structure is often called a \( N \times M \) reconstruction. Strictly speaking, a vicinal surface does not have a periodic lattice because the average separation between steps is incommensurate with the bulk lattice. Therefore, reconstructions of vicinal surfaces are considered to occur on the high symmetry terraces between the steps.

The atomic positions of the 7 × 7 reconstruction on Si(111)[51] are shown in figure 1.3(b). The periodicity is seven lattice units (LU) or about 46Å in the \( \langle 11\overline{2} \rangle \) direction. The three triangular outlines highlight the translational symmetries. The
reconstruction involves the top 1 1/2 bilayers of the surface. The third layer of atoms is modified by the removal of atoms at the vertices of the triangles. The second layer has a reduced density of 42 atoms per 49 \( LU^2 \) at the positions indicated by the open circles in figure 1.3(b) while the top layer has a reduced density of 12 atoms per 49 \( LU^2 \) at the positions indicated by the large closed circles in figure 1.3(b). The atoms present in the top bilayer resemble triangular domains of A and B bilayers in the stacking sequence XCABC...

1.5 Thermodynamics of Vicinal Surfaces

Since the equilibrium behavior of a vicinal surface is determined by the surface free energy density, which can often be modeled theoretically, the equilibrium behavior is the natural starting point for understanding surface properties. The connection between the equilibrium crystal shape (ECS) and the mesoscopic stability of vicinal surfaces is made via the Wulff construction. The ECS can be interpreted as a phase diagram which classifies the transitions from curved stepped regions to flat facets on a crystal surface as either first or second order phase transitions. For a second order transition, the critical behavior is characterized by the related critical exponents of the free energy and ECS profile. The critical exponent of the free energy is determined by the free energy of step interactions. In addition, the reconstruction of a facet can modify the ECS and the stability of vicinal surfaces.

1.5.1 Wulff Construction of the ECS

The thermodynamics of vicinal surfaces is related to the equilibrium crystal shape (ECS). However, the stability of a vicinal surface is found by minimizing the surface free energy subject to a fixed macroscopic surface orientation, whereas the ECS is found by minimizing the surface free energy subject to a constant volume. The ECS is concisely expressed in the Lagendre transformed free energy

\[
H = \min_{\tilde{m}} \int \left[ F(\tilde{m}) \tilde{m} - pR_{ECS}(\tilde{h}) \tilde{h} \right] \cdot d\tilde{S} \tag{1.1}
\]
where $R_{ECS}(\hat{h})$ is the crystal radius, $\hat{h}$ is the surface radial direction and $\hat{m}$ is the surface normal or orientation and $p$ is proportional to the pressure difference on opposite sides of a finite crystal at equilibrium which arises physically from the surface tension.

The relationship between $R_{ECS}(\hat{h})$ and $f(\hat{m})$ given by equation 1.2 is illustrated graphically by the Wulff Construction shown in figure 1-3(a). After plotting $f(\hat{m})\hat{m}$, the crystal radius vector, $R_{ECS}(\hat{h})\hat{h}$, is found by taking the inner envelope of all planes perpendicular to $\hat{m}$ and containing $f(\hat{m})\hat{m}$. The ECS is everywhere curved except at cusps in $f(\hat{m})$. Since $R_{ECS}(\hat{h})\hat{h}$ is a type of free energy, the borders between flat facets and curved stepped regions mark phase transitions.

The transitions from curved regions to flat facets which are discontinuous in $\hat{m}$ mark first order phase transitions whereas those which are continuous in $\hat{m}$ mark second order phase transitions. For first order transitions, sharp edges on the ECS imply that a certain range of surface orientations are excluded at equilibrium. Therefore, a vicinal surface with a macroscopic orientation in the excluded range is unstable and phase separates into regions with local orientations bordering the excluded range. On the other hand for second order transitions, smooth edges exclude no orientations so that all vicinal surfaces are stable. The profile of a curved region near the edge of a flat facet has the form $z(x) \sim -x^\theta$ where $\theta$ is a critical exponent.

### 1.5.2 Free Energy of Vicinal Surfaces

In cases where a non-zero amount of free energy is localized at the steps, it is convenient to study the thermodynamic function $f(\hat{m}) \rightarrow f(c)$ which is more simply related to the properties of steps. This transformation of the free energy was presented rigorously by Ellen Williams[55]. The free energy of an unreconstructed surface as a
(a) Wulff Construction of the ECS

(b) ECS Modified by the 7x7 Reconstruction

Figure 1-3: Wulff Construction
function of step density, \( c \), can be expressed as

\[
f_{1\times1} = f_o + \eta c + gc^\lambda + H.O.T.
\]

where \( f_o \) is the free energy of the flat surface, \( \eta \) is the step energy, and the last two terms represent the interactions between steps.

The sign of \( g \) determines whether \( f_{1\times1} \) has an inflection point and the type of transition on the ECS. By the usual thermodynamic arguments, an inflection point in \( f_{1\times1} \) will cause a first order phase transition (a sharp edge) on the ECS. Attractive step interactions produce a negative \( g \) and an inflection in \( f_{1\times1} \). This results in a sharp edge on the ECS or step bunching on a vicinal surface. On the other hand, repulsive step interactions produce a positive \( g \) and no inflection point in \( f_{1\times1} \). This results in a smooth edge on the ECS or a stable homogeneous step density on a vicinal surface. For second order transitions, the critical exponents of \( f(c) \) and \( z(x) \) are related by \( \theta = \lambda/(\lambda - 1) \) which follows from the Wulff construction and some geometric reasoning.

Examples of repulsive step interactions which contribute positively to \( g \) are entropic, elastic, and repulsive dipole interactions. Examples of attractive step interactions which contribute negatively to \( g \) are attractive dipole interactions. Dipole interactions may be important on metal surfaces, but are not expected to be important on semiconductor surfaces for which the electrons are more localized. Therefore, the transition from the Si(111) facet is expected to be second order.

1.5.3 The Reconstruction on the ECS

In general, the surface of a crystal at equilibrium can have reconstructed and unreconstructed orientations simultaneously. In addition, reconstructions can produce sharp edges on the ECS which would not be present in the absence of the reconstruction. The new ECS with reconstructed and un-reconstructed regions will be referred to as a global ECS (ECS\(_g\)) whereas the ECS of a crystal constrained to have a single terrace structure will be marked by the structure periodicity (e.g. ECS\(_{1\times1}\)).
ECSg can be found by a generalization Wulff construction. Since a reconstructed vicinal surface has a separate free energy function similar to equation 1.3. The observed ECSg is found by taking the minimum of the unreconstructed ECS1x1 and the reconstructed ECS7x7 for each radial direction of the crystal. Figure 1-3(b) shows the behavior of ECSg, ECS1x1, and ECS7x7 below $T_c$. On ECSg, the (111) facet is reconstructed while the stepped regions remain un-reconstructed. A sharp edge occurs at the boarder between these regions.

### 1.5.4 The Reconstruction on Vicinal Surfaces

Reconstructions can also cause mesoscopic faceting on vicinal surfaces due to differences in the step energies. For example, since atomic steps on 7 × 7 reconstructed surface have a higher energy than on the un-reconstructed surface, the reconstruction can cause a vicinal surface to phase separate into low step density, reconstructed regions and high step density, un-reconstructed regions. The phase separation temperature $T_o < T_c$ depends on the average step density.

The free energy functions of the 7 × 7 reconstructed surface, $f_{7x7}$, and a 1 × 1 un-reconstructed surface, $f_{1x1}$, are illustrated in figure 1-4(a) for $T > T_c$. For a macroscopic surface orientation with $c_{band} < c_{macro}$, the surface free energy is minimized by the separation of the surface into 1x1 regions with step density $c_{band}$ and 7 × 7 regions with step density $c_{7x7} = 0$. For $c_{macro} > c_{band}$, the surface remains an unreconstructed single phase with free energy equal to $f_{1x1}(c_{macro})$. The phase separation temperature, $T_o$, is defined where $c_{band}(T_o) = c_{macro}$. On a phase separated surface, the average surface free energy is given by the tie-line at $c_{macro}$. The tie-line intersects $f_{1x1}$ tangentially at $c = c_{band}$ and intersects $f_{7x7}$ at $c = 0$. The fractional areal coverage, $y$, of the surface by the 7 × 7 reconstruction is given by $y = 1 - c_{macro}/c_{band}$.

The following trick for measuring ECS1x1 was first used by N.C. Bartelt et al[4]. Below $T_o$, the step band density follows the unreconstructed equilibrium crystal shape, ESC1x1. Therefore, the 7 × 7 reconstruction driven faceting can be used as a device to study the profile of ECS1x1. Since the 1 × 1 → 7 × 7 reconstruction on a (111)
(a) Phase Separation Due to the 7x7 Reconstruction

(b) Step Density as a Function of Finite-Size Field

Figure 1-4: Vicinal Surface Free Energy
facet is a first order phase transition, the difference in the free energies of the two phases, $\Delta f = f_{1\times 1} - f_{7\times 7}$, near the transition should be proportional to the reduced temperature, $\tau = (T_c - T)/T_c$

$$\Delta f \sim \tau.$$ (1.4)

Using this relation, the critical behavior of the step band density, $c_{\text{band}} \sim \tau^\alpha$, can be derived from either the free energy functions of figure 1-4(a) or the ECS's in figure 1-3(b). From the free energy curves one obtains $\alpha = \lambda$ which relates the critical exponents of the step band density and surface free energy. This provides the most direct means of relating theoretical predictions to experimental results on vicinal surfaces.

1.6 Phase Separation and Phase Convergence

Thus far, the theoretical framework for interpreting the equilibrium behavior of vicinal surfaces has been presented. However, in order to evaluate equilibrium measurements critically, it is necessary to be aware of the non-equilibrium aspects of phase separation. In addition, phase separation is interesting in itself and can be studied experimentally. Therefore, an introduction to phase separation is given here. The term "phase separation" will be used to describe the process in which a single phase becomes two phases while the term "phase convergence" will be used to describe the process in two phases converge to become a single phase.

1.6.1 Mechanisms of Phase Separation

According to the thermodynamics of phase separation, the free energy released by the bulk phase separation must be greater than the free energy required to create the interfaces between the phases. The interfaces may form by either nucleation or spinodal decomposition depending on the free energy functional at a given temperature. The conceptual framework for understanding these mechanisms is given in a review article by Cahn[7]. In this section, these mechanisms are discussed and applied to
the 7 x 7 reconstruction driven faceting.

In order for a phase separation to occur, there must be a driving mechanism for moving constituents from a low concentration to a high concentration. During nucleation, this mechanism is provided by adsorption at the interface whereas during spinodal decomposition, this mechanism is provided by diffusion in the mother phase. During nucleation, the interface is formed first by thermal excitation. Then, the nucleated phase grows according to the kinetics at the interface and diffusion in the mother phase where the diffusive flux is directed down the concentration gradient. In contrast, during spinodal decomposition, diffusion takes place first where the diffusive flux is directed up the concentration gradient. After sufficient mass transport has occurred, the interfaces sharpen in the regions of high concentration gradient.

The direction of a diffusive flux, \( \vec{F}_{\text{diff}} \), relative to a concentration gradient is related to the sign of the diffusion coefficient, \( D \),

\[
\vec{F}_{\text{diff}} = -D \nabla c. \tag{1.5}
\]

According to mass conservation, the time dependent concentration obeys the differential equation,

\[
\frac{\partial c}{\partial t} = -\nabla \cdot \vec{F}_{\text{diff}} = D \nabla^2 c. \tag{1.6}
\]

From this equation, it is easy to see that for \( D > 0 \), a homogeneous phase is stable whereas for \( D < 0 \), a homogeneous phase is unstable with respect to spinodal decomposition. The diffusive flux is determined by the gradient of the chemical potential,

\[
\vec{F}_{\text{diff}} = -M \nabla \mu, \tag{1.7}
\]

where \( M \) is the constituent mobility. Since \( \mu \equiv \partial f / \partial c \), it follows that

\[
\vec{F}_{\text{diff}} = -M \partial^2 f / \partial c^2 \nabla c \tag{1.8}
\]
and

\[ D = M \partial^2 f / \partial c^2. \]  

(1.9)

Therefore, the mechanism of phase separation is determined by the convexity of the surface free energy where negative convexity results in spinodal decomposition. The inflection points in the free energy are called the spinodal and the associated temperatures are called the spinodal temperatures, \( T_{sp}'s \).

In the case of reconstruction driven faceting, this discussion needs to be generalized since the free energy is composed of two separate functions. The generalized free energy, \( f = \min\{f_{1x1}, f_{7x7}\} \), is discontinuous at the point where \( f_{1x1} = f_{7x7} \). For repulsive step interactions, \( f \) has a positive convexity everywhere except at this point. The diffusion coefficient, \( D_{step} \), is associated with the motion of steps. At the point of discontinuity, \( D_{step} = -\infty \) which causes the surface to be unstable with respect to spinodal decomposition. Therefore, the point where \( f_{1x1} = f_{7x7} \) is the spinodal. \( T_{sp} \) occurs where the concentration at the spinodal, \( c_{sp} \), equals the macroscopic concentration, \( c_{macro} \), of the vicinal surface. \( c_{sp} \) is marked in figure 1-4 (a) In summary, faceting occurs by nucleation for \( T_{sp} < T < T_o \) and by spinodal decomposition for \( T < T_{sp} \).

1.6.2 Rates of Phase Separation

The rate of phase separation depends on the faceting mechanism. In spinodal decomposition, the phase separation begins instantly, but its rate of progression is limited by diffusion. The limitations of mass transport and energetics cause a particular mode with a finite wavelength, \( L_w \), to grow most rapidly. According to equation 1.6, initially each mode grows exponentially with a rate \( R_k \sim 1/L_w^2 \). However, as the concentrations gradients become large, higher order terms due to the energetics of stress contribute to limit the growth of short wavelength modes. This causes a particular facet size to be selected initially. Cahn[7] argued that observing the rate of phase separation far below \( T_{sp} \) is difficult in practice because of the limitations of cooling rates and the rapid rate of separation near \( T_{sp} \). He suggested that the most
promising method of obtaining reproducible experimental results below $T_c$ is to take measurements while repeatedly cooling the system at fixed rates.

During nucleation, the rate of phase separation depends on the occurrence of fluctuations. The rate of occurrence of these fluctuations depends on their energy and wavelength. Large wavelength fluctuations form slowly due to the limitation of mass transport whereas small wavelength fluctuations usually decay instead of grow due to their high energy. Therefore, there exists an intermediate wavelength which forms most rapidly. After nucleation, single isolated facets will grow indefinitely according to mass transport. Mullins[40] treated the growth of individual facets for three mass transport mechanisms. In each case, the facet width increases as a power law of time, $t^n$. For the mechanisms of evaporation/condensation, volume diffusion, and surface diffusion, $n$ was found to be 1/2, 1/3, and 1/4 respectively.

After phase separation has occurred over the entire surface, a large amount of phase interface may exist due to the finite average facet size. This interface may be reduced by coarsening. Figure 1-4(b) shows the free energy of the reconstructed and unreconstructed phases as a function of a hypothetical finite size induced field, $H_f$, (e.g. stress near the surface generated by the surface profile). On short time scales, the local phases are constrained by the free energy curves for the local value of $H_f$. However, on longer time scales, mass transport can cause the local length scale to increase and the local field value to decrease. The free energy curves in figure 1-4(b) are drawn such that $c_{\text{end}}$ increases with facet size. This argument applies to both spinodal decomposition and nucleation. Most theories of coarsening predict that the facet sizes continue to follow a power law growth rate similar to isolated facet growth, however the time scale is much longer for coarsening[53].

1.6.3 Mechanisms of Phase Convergence

Phase convergence can also occur at equilibrium or at non-equilibrium. Equilibrium convergence occurs when mass transport is rapid with respect to the motion of the equilibrium state and in the absence of hysteresis. Hysteresis which is caused by energy barriers to convergence is an example of non-equilibrium phase convergence.
Hysteretic convergence on vicinal surfaces can occur in the presence of intrinsic defects or extrinsic impurities on the surface which cause the steps to become pinned. While equilibrium phase convergence occurs at \( T_0 \), nonequilibrium phase convergence occurs at temperatures above \( T_0 \).

### 1.7 Non-Equilibrium Step Flow

At sublimation temperatures, the equilibrium properties become less relevant as the step begin to flow due to the recession of the surface. For these cases, it is useful to formulate the stability of step flow. Here we expand on the discussion given by F.C. Frank[12]. Frank pointed out that this formulation is identical to a treatment of traffic flow and river flow given by Lighthill and Whitham[36]. The step bunching instability on vicinal surfaces is analogous to traffic jams on roads and the flooding of rivers.

The stability of the surface under step flow can be determined by a differential equation describing the step flow. In the continuum approximation, the steps will satisfy the conservation relation

\[
\frac{\partial k}{\partial t} = -\frac{\partial (kV_{\text{step}})}{\partial x}
\]  

(1.10)

where \( k = 1/l \) is step density and \( V_{\text{step}} \) is the step velocity. For simplicity, it is assumed that the total number of steps is fixed, therefore no source term occurs in equation 1.10. Frank discussed the stability of cases where the step velocity is function of the step density. Here, a generalization is made by assuming that the step velocity also depends on the gradient of the step density, \( k_x \) (i.e. \( V_{\text{step}} = V_{\text{step}}(k, k_x) \)) where the subscript, \( x \), refers to the partial derivative. Equation 1.10 becomes

\[
\frac{\partial k}{\partial t} = D_{\text{step}} \frac{\partial^2 k}{\partial x^2} - V^* \frac{\partial k}{\partial x}
\]  

(1.11)

\[
V^* = V_{\text{step}} + k \frac{\partial V_{\text{step}}}{\partial k}
\]  

(1.12)

\[
D_{\text{step}} = -k \frac{\partial V_{\text{step}}}{\partial k_x}
\]  

(1.13)
In analogy with spinodal deposition, the stability of the surface is determined by the sign of a diffusion coefficient. If $D_{\text{step}} > 0$, the surface is stable whereas if $D_{\text{step}} < 0$ the surface is unstable. The step velocity $V_{\text{step}}(k, k_x)$ is found from a specific model of step-flow.
Chapter 2

Experimental Techniques

2.1 Introduction: Faceting at a Hot-Spot

During early x-ray studies of the 7 × 7 reconstruction on vicinal Si(111), resistive heating was chosen to control the sample temperature for the reasons described below. However, since the current driven instabilities were unknown, the direction of current flow was not expected to be significant. During these experiments, heating the sample to high temperatures to drive off impurities provided highly unpredictable results. On some occasions, x-ray diffraction from the steps produced sharp peaks above $T_c$ indicating a very well ordered step phase. On other occasions, the step peak was either very broad or undetected above $T_c$ indicating that the steps were disordered. The occurrence of these two phenomena seemed random. It was not until the relevance of the high temperature non-equilibrium instabilities was recognized that rapid progress could be made.

The first indication of the high temperature instabilities came from a sample which had obtained a cloudy appearance in the region of a hot-spot near one of its electrical contacts. Hot-spots are regions of the sample that become hotter than the surrounding regions due to non-uniform heating. The presence of the hot-spot prevented the use of short anneals (flashes) above 1200° C to clean the central region of the sample exposed to x-rays. Generally, it is believed that heating the sample above 1200° C is required to drive off carbon impurities from the surface.[26] (A study of
flashing is presented in chapter 3.) Instead, a longer anneal at a lower temperature was used to prepare the surface.

The cloudy appearance suggested the presence of micron sized topological features on the surface. Optical microscope images of the surface in atmosphere revealed large facets about 5 – 10μ in size. Figure 2.1(a) and (b) show corresponding scanning electron microscope (SEM) photographs taken a few millimeters apart along a gradient of the cloudy region. The long dimension of this sample is 30° from the <112> direction which accounts for the 60° angle between the faceting direction and the sample edge. The region of figure 2.1(a) was exposed to higher temperatures than the region of figure 2.1(b). These images show that ~6μ facets formed in the cooler regions and ~9μ facets formed in the hotter regions. The facets formed in the hotter regions appear sharp while the facets formed in the cooler regions appear less sharp and may not in fact be true facets. At the higher temperatures, the facets also show a wavy structure with a periodicity of ~7μ as shown in figure 2.1(a). This wavy structure provides intuitive evidence of a dynamic instability as opposed to an equilibrium instability.

The sizes the observed facets suggest that optical methods can be useful in studying the surface topology. While microscope images provide satisfying detail of the topology, they are difficult to obtain insitu. Therefore, the potential of using laser diffraction was explored. The sample of figure 2.1 was mounted on a four-circle diffractometer with a low power (2 milliwatt) HeNe alignment laser beam directed at the center of rotation. Then the sample was translated to expose various faceted regions to the 2 mm diameter laser beam. In this configuration, the diffraction pattern visible on the walls of the room appeared as a long streak in the <112> direction.

In order to record the diffraction intensity, a photocell was taped to the wall with electrical leads attached to a current meter through a small resistor. The sample was aligned such that a single diffractometer motor could be used to sweep the diffraction pattern across the photocell. With the room lights off, scans were taken for several regions of the sample. Figure 2.1(c) and (d), shows the scans for the regions corresponding to the images in figure 2.1(a) and (b) respectively. The smaller facets
Figure 2-1: Images and Laser Diffraction of a Hot-spot
produced multiple diffraction peaks with a spacing of about 3.5° indicating a periodicity of ~ 5μ whereas the larger facets produced broad specular peaks from the (111) facets and the step bands.

From these results, it is clear that laser light can provide useful information concerning the surface topology. Therefore, the laser diffraction technique was further developed for systematic in situ studies. A description of this technique is given below.

Since the cloudiness in the region of the hot-spot was not noticed until after the sample was cooled to room temperature, the conditions which caused the faceting were not completely certain. The production of similarly cloudy surfaces seemed to develop randomly in previous experiments, however in this case, presumably, the hot-spot became cloudy during the cleaning process. Later experiments support this conclusion.

Given that the facets developed at high temperature, it is also clear from the history of the sample that the facets are stable for many hours at temperatures near Tc. In our studies of the equilibrium crystal shape, an important assumption is that the macroscopic surface orientation is conserved during the reversible phase separation. The presence of frozen macroscopic facets formed at high temperatures could compromise this conservation principle. Therefore, understanding the high temperature stability of vicinal Si(111) is a prerequisite to studying the equilibrium crystal shape.

The common occurrence of hot-spots indicated the need to improve the sample heating technique. In order to study the high temperature stability, it is desirable to study the sample for hours or days at flashing temperatures. The presence of hot-spots due to non-uniform heating prevents these kind of studies. In the remainder of this chapter various experimental techniques and apparatus are discussed. They include improved sample mount and temperature control, the decoupling of the sample temperature from the D.C. voltage applied across the sample, and the development of an in situ laser diffraction technique.
2.2 X-ray Diffraction

Our x-ray experiments were performed at Brookhaven National Laboratory (BNL) in Professor Simon Mochrie's UHV surface chamber which was built by Doug Abernathy. The properties of the x-ray beam are determined by the BNL synchrotron ring and the X20A beamline[48]. The x-rays are produced by the acceleration of high energy electrons at the X20 bending magnet. The beam is narrowed by slits before being focused by reflection off of a gold mirror. The focal point is set at the sample position. However before reaching the sample, the beam is filtered to a narrow energy distribution using a double-bounce Ge(111) monochromator. The arrangement of the focusing mirror and the monochromator is shown in figure 2-2(b). In these experiments, the x-ray energy was set close to 8.1 keV ($\lambda \approx 1.5\text{Å}$), near the Cu $K_{\alpha}$ cutoff energy.

After leaving the monochromator, the incoming x-ray beam is further defined by slits. The outgoing beam is defined by slits on the $2\theta$ arm of the diffractometer. The incoming and outgoing beam intensities are measured using Bicron scintillation detectors and counting electronics. Due to the variable current in the synchrotron electron ring, the outgoing beam intensity is usually normalized by the incoming beam intensity (normalized by monitor).

The distribution of steps on a vicinal surface can be studied by measuring the x-ray scattering intensity along the surface truncation rods. A crystal surface can be modeled as a truncation of a crystal lattice. The effect of the truncation on the Bragg diffraction peaks is to create slowly decaying tails along the surface normal. Measuring the tilt of these tails allows one to determine the orientation of the surface normal. More generally, if a vicinal surface is unstable, the truncation rods will split up into components indicating the distribution of step densities. In our experiments, we measured the distribution of the truncation rod of the (111) Bragg peak. Measurements were made along the $<1\bar{1}2>$ direction in the plane parallel to the $\{111\}$ atomic planes. This region of reciprocal space was selected in order to minimize the background scattering from the bulk.
Figure 2-2: Grazing Incidence X-ray Scattering
In discussions of these experiments, it is useful to introduce a surface coordinate system where the coordinate axes, (1,0) and (0,1) in the \{111\} plane are along the \(<11\bar{2}>\) and \(<\bar{1}\bar{1}0>\) directions respectively. It is convenient to choose the scale such that the (1\bar{1}1) Bragg peak resides above the (1,0) surface position. Then the truncation rod of the (1\bar{1}1) Bragg peak creates surface peaks near the (1,0) position. The \(<22\bar{4}>\) bulk Bragg peak is equivalently described as the (3,0) Bragg Peak. In addition, the (0,1) unit vector is scaled in order to correspond to the \(<\bar{1}1\bar{0}>\) Bragg peak.

X-ray measurements were made using grazing incidence scattering geometry as shown in figure 2-2(a). While studying the (1,0) surface peak, the momentum transfer, \(\Delta k\), is roughly parallel to the \(<11\bar{2}>\) direction. However due to the small miscut toward the \(<11\bar{2}>\), \(\Delta k\) lies slightly above the surface. The incoming and outgoing x-ray beams are also slightly above the surface.

In x-ray scattering experiments, the resolution function determines the maximum domain over which correlations can be measured. In our experiments, the total instrument resolution is determined by a combination of many factors associated with the incoming beam and outgoing detector flight-path. Since these factors combine in a complicated way, in practice, one usually resorts to measuring or approximating the resolution function.

One method of approximating the resolution function is to measure the shape of the scattering profile at a bulk peak and then translating that profile to the surface peak position. The dotted lines in figure 2-3(a) show the half maximum contours of the (3,0) Bragg peak. The long axis of the ellipse is determined by the slits on the detector arm which were set to allow a 0.15° angular acceptance in the scattering plane. The length of this axis is independent of position in reciprocal space.

The shorter axis of the ellipse is more difficult to translate. The simplest translation is to scale the \(\Delta K\) width by the value of the \(H\) coordinate so that the transverse angular widths, \(\Delta \theta_t\), are equal. The dotted line in figure 2-3(b) shows the half maximum contour of the translated bulk peak profile with \(\Delta K_{(1,0)} = \Delta K_{(3,0)}/3\). This translation proved to underestimate the true resolution. Figure 2-4 shows the \(\theta\) scans.
Figure 2-3: X-ray Resolution
of the (3,0) peak and the sharpest measured (1,0) surface peak. One can see that the (1,0) surface peak is sharper in the transverse direction than the (3,0) bulk peak.

On the other hand, a scan of the down-stream monochromator crystal at arm-zero (no momentum transfer at the sample) provides an adequate approximation of the transverse resolution. The solid lines in figure 2-3 show the resulting resolution half-maximum contours.

The fact that the width of the monochromator scan provides an acceptable resolution width at the (1,0) position but not at the (3,0) position is probably related to the monochromator spacing, \( d_{Ge(111)} = 3.266 \text{Å} \). This spacing is comparable to the (1,0) spacing, \( d_{(1,0)} = 3.254 \text{Å} \), but is quite different from the (3,0) spacing, \( d_{(3,0)} = 1.085 \text{Å} \). This means that at the (1,0) position, the sample and monochromator are in an almost perfectly non-dispersive scattering configuration whereas at the (3,0) position, they are in a partially dispersive scattering configuration.

The tilted axes of the resolution function is somewhat inconvenient for deconvolving the scattering function from the lineshape. These deconvolutions are performed by using fitting algorithms. Obtaining the 2-dimensional scattering functions from the lineshapes generally requires a large amount of computation due to the large integration domains. Therefore, few 2-dimensional deconvolutions have been attempted. On the other hand, peak widths can often be interpreted by merely knowing the resolution limit. Therefore, a discussion of the resolution limits is given below.

The measured x-ray surface peaks near the (1,0) position are often resolution limited in either the \(<1\bar{1}2>\) (longitudinal) or \(<1\bar{1}0>\) (transverse) directions or both directions. For a tilted resolution function as shown in figure 2-3, the resolution limit in each direction is a function of the shape of the x-ray peak. For example, the longitudinal resolution limit for a scattering function with a delta function transverse profile is about \(3 \times 10^{-4} \text{ R.L.U.}\) whereas for a scattering function which has a flat transverse profile, the longitudinal resolution limit is about \(5 \times 10^{-3} \text{ R.L.U.}\). An analogous relationship exists between the transverse resolution limits and the longitudinal widths of the scattering profiles. Figure 2-5 shows the resolution limits as a function of the measured peak widths. Since the surface correlations are generally
Figure 2-4: Transverse Resolution Scans
greater in the transverse direction than in the longitudinal direction, the measured widths usually lie in regions (1), (3), and (4) in figure 2-5. Step peaks are not usually longitudinally resolution limited and therefore, lie in regions (3) and (4) whereas facet peaks are usually transversely limited and therefore, lie in regions (1) and (3).

2.3 Laser Reflection Diffraction

Laser diffraction studies were made using three experimental configurations. The laser diffraction patterns could be studied either quantitatively or qualitatively. Qualitative studies consisted of visual observations of the diffraction patterns to determine the micron-scale morphology of the surface. The quantitative studies were performed using a lightmeter with a HeNe laserline bypass filter to record the diffraction profile.

In one configuration, the sample is first annealed in UHV at a particular temperature with a particular heating scheme. The sample is then quenched to room temperature and studied on a Huber four-circle diffractometer in atmosphere. These studies are conveniently combined with imaging techniques.

In a second configuration, the sample is studied in UHV with both x-rays and laser light simultaneously. This allows the laser and x-ray diffraction data to be correlated. These experiments took place at Brookhaven National Laboratory in the Professor Simon Mochrie's UHV surface chamber. The laser study was facilitated by an 8" viewport roughly parallel to the sample surface in grazing incidence x-ray scattering geometry. The laser configuration is illustrated in figure 2-6.

In these studies, the laser light momentum transfer vector was fixed due to the fixed locations of the laser and lightmeter. The scattering angle was typically within 3° of 180°. The diffraction profile was scanned by rocking the crystal along the symmetry axis of the laser diffraction pattern. These rotational axes were provided by the same diffractometer used during the x-ray studies.

The third experimental configuration is similar to the above configuration. However, the experiments are performed using a UHV system dedicated to optical studies. Such a UHV system was constructed from equipment stored in our lab. Most quan-
Figure 2-5: The X-ray Resolution Limits
Figure 2-6: Laser Reflection Diffraction
titative in situ laser studies were performed using this system. The UHV chamber in this system has many conveniently located ports suitable for these studies. Two 8" ports were equipped with viewports to allow optical studies to be performed. For these studies again the momentum transfer vector was fixed due to the stationary laser and detector. To measure the diffraction profiles, the crystal could be rocked on two-axes which were aligned along the diffraction symmetry axes. The rotations of the sample were provided by a double axes sample manipulator mounted on a double axes rotary feedthrough. This sample manipulator was originally designed and built by Elliot Specht and was used for years on the "R2D2" UHV surface chamber built by Allen Mak, and Do Young Noh.

2.4 Resistive Heating

A number of heating schemes can be used to control the temperature of Si samples in UHV. Among the most common are resistive heating, conductive heating, radiative heating, and electron beam heating. Some of the criteria for selecting a particular heating method are surface cleanliness, temperature uniformity, and simplicity. In our studies, resistive heating was used due to the increased cleanliness, the convenient sample geometry and the ability to produce sample mount parts in shop. On the other hand, obtaining temperature uniformity can be challenging while using resistive heating.

Resistive heating results from passing an electric current through the bulk of the sample. The electrical resistance of the sample generates heat which is dissipated by radiative and conductive heat loss. This provides the smallest level of outgassing from the sample and sample mount for a particular temperature since the hottest element is the sample itself. The low level of outgassing reduces the occurrence of surface contaminants.

In resistive heating, there are a number of factors which determine the uniformity and stability of the sample temperature. Ideally, the conductive heat loss is equal on each end of the sample. Then the temperature profile is symmetric about the
center of the sample. In our x-ray studies, the x-rays illuminated a region near the center of the sample. Therefore, for symmetric heat flow, the width of the sampled temperature range depends on the conductive losses in the second order. On the other hand if the symmetry of the heat flow is lost, the width of the sampled temperature range depends on the conductive losses in the first order.

A second major factor determining the symmetry of the heat flow is the uniformity of the electrical contacts across the width of the sample. With non-uniform contact, the current flow is non-uniform across the width of the sample. As the current begins to flow preferentially at high pressure points, the temperature near the high pressure points increases more rapidly than the surrounding regions. The higher temperature lowers the local resistivity which causes greater preferential current flow through these regions. The resulting hot-spots tended to become progressively more pronounced and problematic over time as the sample becomes thinner due to sublimation. For the sample in figure 2.1 the hot-spot prevented the proper cleaning of the center of the sample. In the worst cases, hot-spots can cause the sample to melt before the central region of the sample can be heated to a desired temperature.

2.5 Sample Mount

The sample mount used in these experiments is shown schematically in figure 2-7. this design is based on the sample mount built by Allen Mak. The essential features are a long narrow sample with electrical contacts made near the sample ends through small pieces of Si wafer (sandwich pieces). The design of Mak also incorporated an alignment pin directly below the sample center.

In grazing incidence scattering geometry, a long sample dimension is required to allow incoming and outgoing paths for the x-ray beam. The sample dimensions are typically 1.3" x 3" x 15 mils where the long dimension is cut along the \( <11\bar{2}> \) direction parallel to the miscut such that the steps run across the width of the sample. This orientation is convenient for DC current resistive heating studies where electrical contacts on the ends of the sample allow current to flow in the step-up or step-down
directions.

A major source of temperature non-uniformity is the non-uniformity of electrical contact across the width of the sample. The electrical contacts are made by applying pressure to metal foil in contact with the Si sandwich pieces. The sandwich pieces are useful in distributing the current evenly across the width of the sample. The sandwich pieces also reduce the average current density such that the sample ends are cooler than the sample center. This reduces the effects of non-uniform electrical contacts. Due to the large amount of sample sublimation which occurs at temperatures near the melting point, the metal foil pieces often become fused with the Si pieces therefore, the foil pieces need to be replaced regularly.

In the present sample mount, the sample was electrically isolated from the Ti base plate by alumina spacers and collars. The Ti base provided for parallel alignment of the sample clamps which is required to limit the stress on the sample. The base also provided a platform to mount the centering pin and thermocouples, (TC's). The electrical leads were made of woven copper wire threaded through insulating sleeves. The electrical leads were attached to Mo foil strips extending out from the sample such that the copper leads and isolating sleeves did not get too hot. The stainless steel base plate, shown in figure 2-7, is welded to a post extending from a 6" Conflat flange. During experiments, the flange is mounted onto a 6" port of the UHV chamber.

The construction of the sample mount in figure 2-7 is much different from that of the mount built by Allen Mak however, there are only a few functional differences. In the mount shown in figure 2-7, the pressure is applied by Mo clamps instead of Ta clips. The Mo clamps are operated with four stainless steel screws instead of two screws for the Ta clips. This modification was made in order to standardize the sample length which allows simpler comparisons of the heating behavior between samples. However with the use of clamps, care must be used in tightening the screws evenly in order to achieve uniform pressure.

In addition, the method of attaching thermocouples (TC) was modified. It had been the practice to spot weld TC wires to various portions of the sample mount. This technique was replaced by spring mounting commercial TC's under the sample
Figure 2-7: Sample Mount
next to the alignment pin. Two or three thermocouples could be used to measure the temperature profile along the length of the sample. If a TC was placed in the center position, it also served as an alignment pin.

### 2.6 Temperature Control

Controlling the sample temperature during resistive heating of semiconductors is most easily accomplished using a current regulated power supply. Figure 2-8 shows the voltage and current across a sample as a function of heating power and sample temperature. The sample temperature as a function of heating power is specific to the sample geometry and rate of heat dissipation. A voltage source can be used to heat the sample in the ohmic region which for our samples is below about 10 V. However, above about 10 V, the sample will eventually melt due to thermal run-away. On the other hand, the current supplied to a semiconductor sample provides a reproducible measure of the temperature as long as the heating profile remains fixed.

In some cases, it is convenient to implement feedback temperature control. Under conditions of rapid sublimation, the sample resistance changes over time causing the sample temperature to drift upward for a constant current. A temperature feedback signal can be used to adjust the current downward to maintain a constant sample temperature. Also, if DC resistive heating is combined with another source of heating, then feedback is useful in controlling the sample temperature.

A current regulated power supply is also required during feedback control of the sample temperature. In figure 2-8, note that between 500°C and 1300°C, the voltage has either a negative slope or is nearly constant near 10 V. The negative slope results from the delayed response after the temperature has adjusted to its steady-state value. On the other hand, the instantaneous response has a positive slope due to the positive sample resistance. The opposite signs of the delayed and instantaneous responses indicates that unstable behavior will occur if feedback is implemented using a voltage regulated supply. On the other hand, the sample current provides stable control of the sample temperature.
Figure 2-8: Sample Voltage and Current vs Power and Temperature
2.7 Temperature Measurement

An optical pyrometer and thermocouples (TC's) provided two traditional methods to measure the sample temperature. In addition, a lightmeter was constructed to provide a temperature feedback signal.

The optical pyrometer provided the most reliable measurements. Our pyrometer readings have a precision of 1° C and are in digital ASCI format. This is convenient for interfacing with the computer from which the experiment is controlled. However, the ASCI format is inappropriate for feedback control. Since the pyrometer measurements were made through a glass viewport on the chamber, precautions were needed to prevent the build up of Si deposits during periods of rapid sublimation. For this purpose, a movable shield was replaced between the sample and the viewport. The viewport was unshielded only during brief periods of temperature measurement.

Thermocouples were also used to measure the sample temperature. The TC contacts were made as described in the section on the sample mount. The TC's produced analog signals on the order of 10 mV which were consistent with the optical pyrometer readings. However, the TC's had several drawbacks. For one, they were very fragile and they often broke before they gave useful readings. Second, the thermocouple were quickly degraded by Si deposits. Third, their signals were weak and susceptible to noise which made them unsuitable for supplying a feedback signal. Fourth, the commercial TC junctions were expensive. The difficulties encountered with the TC's were so severe that they were eventually abandoned as other methods of temperature measurement were developed.

In order to obtain a temperature signal suitable for temperature feedback control, a lightmeter was designed to measure the luminosity of the sample through a glass viewport on the UHV chamber. The physical principles of this method are similar to those of an optical pyrometer except that an optical pyrometer is sensitive to the spectrum of emitted light whereas the lightmeter measures the integrated spectrum intensity of emitted light.

The lightmeter consists of a photodiode, a set of apertures, a telescope housing, a
lens, and an amplifier as shown in figure 2-9. The lens is used to form an image of the sample on the photodiode. The apertures and telescope housing are used to control the image intensity, define the region of measurement on the sample, and to block stray light from reaching the photodiode. The lightmeter was focused and aligned on the sample center by replacing the photodiode with an eyepiece lens which created a telescope. The sample center could be marked with a laser beam during alignment. Then the measured region of the sample surface was selected using apertures.

The photodiode was operated in current mode and connected to the input of a signal amplifier with an adjustable gain of $10^5$ or $10^6$. The output was monitored with a voltmeter and used as a feedback signal. Figure 2-8 shows a typical lightmeter signal as a function of heating power and sample temperature. The lightmeter signal is a much stronger function of temperature than is the sample current. For this reason, the lightmeter signal provides much finer temperature control than does current control and eliminates any temperature drifts due to changes in the heating profile.

Since there was some indication that the noise in the feedback signal caused an increase in the rapid fluctuations in the sample temperature compared to direct control, direct control of the sample current was used at low temperatures where sublimation effects were negligible. However, due to the lightmeter's high sensitivity, it provided a rough monitor of the temperature down to room temperature which was useful while turning the sample on.

In order to reduce the problems associated with the mirroring of the viewport, the luminosity was measured after reflection off of a Si mirror as shown in figure 2-7. This allowed the viewport to be shielded from the sample. It was generally found that the deposition of Si onto the Si mirror did not significantly affect the stability of the feedback signal.

### 2.8 DC Power and Mixed DC and AC Power

Pure DC heating was available using a Hewlett Packard 5030A power supply which could supply 1700 Watts with a maximum current of 17 Amps. This was sufficient
Figure 2-9: Lightmeter
current to heat samples which were 15 mils thick. However when heating samples 20 mils thick, it was necessary to use two HP power supplies in parallel. The second power supply was generously lent by Glen Held at IBM, T. J. Watson Research Center.

A second heating scheme was devised which decoupled the applied DC voltage and the sample temperature. This was useful for studies of the DC dependence of the surface stabilities. This scheme involved combining a DC power supply with an AC power supply. In our studies, we assumed that the AC current or voltage changes are too rapid to affect the surface morphology. A DC power supply was used to select a DC voltage while the AC power supply was used to control the sample temperature. The temperature control is facilitated by using current regulation as in the case for pure DC heating except that now the AC supply is regulated.

A 30 Amp AC current regulated supply was purchased from Superior Electric which consisted of a variable AC transformer with a motorized axis. Current regulation is achieved by using a current transformer to measure the AC output current and then generating a feedback signal to the motor. The temperature feedback was implemented by integrating the temperature signal and sending it to the AC control circuit as the setpoint signal. In combining AC and DC heating, the DC power was supplied by a homemade unregulated power supply. The AC supply was connected to one end of the sample while the DC supply was connected to the other. The resultant sample voltage is shown in figure 2-10 for pure DC heating and DC plus AC heating. In retrospect, the DC plus AC heating may have been implemented more effectively using a high power audio amplifier circuit as pointed out by Nathan Belk.

2.9 Power and Control Circuits

In order to provide flexibility in selecting the type of heating applied to the sample, a power circuit was designed which allowed the polarity of the DC heating current to be switched and for a DC bias to combined with AC heating. High current relays were used to switch the current without significantly disrupting the sample temperature.

The functionality of the power selector is shown in figure 2-10. DC #2 refers to
Figure 2-10: Power Selector
the HP regulated power supply while DC #1 refers to the homemade unregulated DC power supply. A polarity toggle switch is used to activate relays which reverse the connections of the DC power leads. Another toggle switch activates the relays which connect the sample to either DC #2 or DC #1 plus AC. DC #2 and AC are regulated supplies which allow a external setpoint. At any given time, only one regulated supply is connected to the sample in order to prevent unstable behavior.

The control signal for the regulated power supplies is produced by the control circuit shown in figure 2-11. The control type can be either direct or feedback.

In direct control, a fixed signal is produced which determines the current setpoint. The fixed signal is supplied by either an adjustable voltage divider or remotely. For DC #2, an equivalent functionality is provided by the power supply's front panel controls. The front panel controls are disabled while using the control circuit in figure 2-11.

During feedback control, the fixed signal is used as a temperature setpoint signal instead of being directed to the output. A difference amplifier compares the setpoint signal with the temperature feedback signal produced by the lightmeter. The difference is amplified and connected to the output which is sent to the regulated power supply.

Switching the DC polarity can be done without special precautions, however, switching between direct and feedback control must be done with care so that the control signal does not abruptly jump out of an acceptable range. If the current is too high, the sample will melt. In order to facilitate the switching between direct and feedback control, a dial allows various signals internal to the control selector to be read by a voltmeter. Also, an adjustable voltage limiter is provided on the output signal. This protection limit is usually used to override the control while switching between direct and feedback control.
Figure 2-11: Control Selector
Chapter 3

First Experiments

In this chapter, the first experiments which revealed various phenomena are discussed. Data are presented for each of the regions of the phase diagram in figure 1.2.

In March of 1993, we performed our first experiment combining in situ x-ray and laser diffraction. The primary goal of this experiment was to confirm the current related instabilities reported by Latyshev[34, 35]. In addition, we confirmed that the surface morphology formed at high temperatures can become frozen in at low temperatures. The instabilities at high temperatures suggest a specific surface preparation routine. A study of the effects of flashing the sample to various stability regions indicated that the best way to prepare a clean surface with ordered steps was to flash to a high temperature stable region of the phase diagram with current flowing in the step-up direction (negative current). In the course of this study, the current dependent step bunching just above the $7 \times 7$ reconstruction was discovered. The initial study of the current dependence below the $7 \times 7$ reconstruction is also presented in this chapter. In later chapters, more detailed follow up experiments are described.

3.1 Frozen Surface Morphologies

In our first experiment, we began with current flowing in the step-down direction (positive current). Initially, the in situ sample preparations were performed in the traditional style by repeatedly flashing the sample to sublimation temperatures in
order to remove an oxide layer and impurities from the surface. After flashing the sample nine times to 1260 – 1300°C for 30-60 seconds, no surface x-ray peaks were observed near the (1,0) position. A description of the x-ray scattering geometry is given in chapter 2. Next, two 15-minute anneals at 1190°C and 1170°C also failed to produce any surface x-ray peaks. Then, two one-hour anneals at 1130°C and 1170°C were tried, but did not produce any discernible diffraction peaks. Figure 3.1(a) and (b) show x-ray scans taken at 725°C and 1200°C.

The absence of the surface peaks as in figure 3.1 had occurred many times previously with no apparent explanation and with no indication of how to produce an ordered-step peak. However, in this experiment, observations of laser diffraction patterns guided us out of this conundrum.

During the last anneal, we began to notice by eye transverse laser diffraction spots in the <110> direction on both sides of the specular reflection spot. These transverse spots are illustrated in figure 3.1(a). Two orthogonal scans of the laser diffraction profile are shown in figure 3.1(a) and (b). It should be noted that the laser scans in figure 3.1 were taken at 725°C and that the laser diffraction patterns retained their qualitative features during rapid cooling.

Next, two consecutive 10 minute anneals at about 1300°C were performed while monitoring the laser diffraction. During the first of these anneals, two longitudinal laser diffraction spots became visible in addition to a ring-like pattern. This pattern is shown schematically in figure 3.1(b) while the corresponding laser scans are shown in figure 3.1(c) and (d). These scans show the longitudinal peaks and reduced transverse peaks. After the second anneal at 1300°C, the transverse spots had essentially disappeared while the longitudinal spots had increased. This pattern is shown schematically in figure 3.1(c) while the longitudinal diffraction profile is shown in figure 3.1(e). We note that the longitudinal spots became asymmetric over time such that the spot in the <112> direction was smaller and brighter and closer to the specular spot. After improvements were made to the line-up of the laser and photodetector, this asymmetry also became apparent in additional laser scans not shown in figure 3.1.
Figure 3-1: X-ray Profiles for Three Histories
Figure 3-2: Laser Diffraction Patterns
Figure 3-3: Laser Diffraction Profiles
This guided annealing sequence produced dramatic changes in the x-ray surface scattering. Figure 3.1 (c) shows the x-ray surface peaks recorded at 725° C immediately after the previous anneals at 1300° C. Sharp (1,0) and 6/7 th’s surface peaks are present at $H = 1.0$ R.L.U. (reciprocal lattice units) and $H = 6/7 \approx 0.857$ R.L.U. respectively. The (1,0) peak indicates (111) facets are present on the surface while the 6/7 th’s peak indicates that the facets are reconstructed. In addition, there is a step peak between the (1,0) and 6/7 th’s peaks due to a step-bunched phase.

Next, the sample temperature was slowly raised through $T_c$. Below $T_c$, the (1,0) and 6/7 th’s peaks decreased in intensity while the step peak moved toward the (1,0) position. This behavior is consistent with previous observations of un-faceting on vicinal Si(111). On the other hand, above $T_c$, the facet peak became more intense and sharper as demonstrated in figure 3.1(d) at 930° C. This observation of faceting above $T_c$ contradicts previous observations of a single uniform step phase. Here we note that the longitudinal laser spots remained present throughout the scans at these temperatures. This fact indicates a consistency between the x-ray and laser observations of faceting.

In order to test the reproducibility of the high temperature morphological changes, the sample was annealed again at a lower temperature, 1140° C, for one hour. During this anneal, the laser diffraction pattern slowly evolved into a ring-like pattern similar to the one observed earlier. This ring-like pattern remained after cooling the sample. The x-ray scans in figure 3.1(e) and (f) were recorded for 725° C and 930° C sequentially. The scan at 725° C is similar to the corresponding scan shown in figure 3.1(c) except that the step peak is weaker and broader. On the other hand, the scan at 930° C is much different than that of figure 3.1(d). In figure 3.1(f), a well-ordered step peak occurs at the uniform step-density position while only a remnant of the (1,0) peak is present. This last behavior is consistent with the behavior reported by others.[41, 42, 15, 25].

The correlation of the laser diffraction patterns and the current direction with the x-ray diffraction profiles represented a major turning-point in our study. The importance of the laser diffraction data is seen by considering the data in figure 3.1
in the absence of the laser diffraction data. It would seem that the three sets of scans above and below $T_c$ were taken from samples which were prepared in almost identical fashions. A sample which is heated to various temperatures for various lengths of time without the guidance of the laser diffraction patterns would migrate through various states in a seemingly random trajectory. With enough experience, one might expect to notice a correlation between the flashing history and the x-ray profiles however, it turns out that for the opposite current direction, the correlation is exactly opposite. Therefore, without recording both the current direction and the laser diffraction, it is difficult to develop an understanding of the x-ray results.

3.2 Length Scale Measurements

The measurement of lengths is one of the primary quantitative uses of diffraction techniques. Here we summarize the various length scales obtained from the laser scans in figure 3.1 and from the x-ray scans in in figure 3.1. Detailed discussions of the phenomena associated with these lengths is given in later chapters in the context of more systematic studies. Here the object of presenting the lengths obtained from diffraction is to show consistency with the OM and AFM images in figure 2.1.

The HeNe ($\lambda = 0.6328\mu$) laser diffraction data contain information at larger length scales than the $\sim 8.5$ keV ($\lambda =\sim 1.5\AA$) x-ray diffraction data. In figure 3.1, the laser peak separations of about $3^\circ$ and $5^\circ$ correspond to periodicities of $12\mu$ and $7\mu$ respectively. Therefore, the longitudinal step bunching instability occurred at about $7\mu$ while the transverse step wandering instability occurred at about $12\mu$. The widths of the laser diffraction peaks determine the correlation or coherence length of the step wanderings. Although the widths of the peaks in figure 3.1 are less than the peak separation, the coherence lengths are about equal to the periodicity since transforming peak separations to real-space periodicities involves an extra factor of about $2\pi$. The width of the specular spot is a function of the coherence length of the laser beam which in this case is on the order of 1 mm.

In the x-ray data, the maximum detectable length scale is determined by the
instrument resolution. The resolution function in our measurements is described in detail in the previous chapter. The effective longitudinal resolution in our experiments was about 1μ as determined by the monochromator and the slits on the detector arm. Therefore, the morphological features occurring at 5 to 15μ are not detectable by x-rays.

In figure 3.1, the position of the (1,0) peak is related to the separation of the \{11\bar{2}\} atomic planes (\sim 2.17Å). The spacing between the 6/7 th's and (1,0) peaks is related to the periodicity of the 7x7 reconstruction (\sim 23Å). Meanwhile, the spacing between the step peak and the (1,0) peak is related to the step spacing which on a 3° miscut surface is \leq 60Å.

The widths of the x-ray step peaks are related to the step correlation lengths. The scans in figure 3.1(c), (d), (e) and (f) give step correlation lengths of 350Å, 280Å, 220Å, and 750Å respectively. Similarly, the widths of the (1,0) peaks are related to the (111) facet sizes. The minimum facet sizes implied by the scans in figure 3.1(c), (d), and (e) are 4300Å, 7700Å, and 2300Å respectively. These lengths are obtained by assuming Gaussian lineshapes. These length measurements suggest that the unfaceting causes the step correlations to increase whereas the occurrence of large facets above \(T_c\) is accompanied by short step correlation lengths.

### 3.3 High Temperature Current Effected Instabilities

Now turning to the current effect at higher temperatures, x-ray data were collected at various temperatures between 1100° C and 1300° C with positive and negative current. Distinctly different surface morphology was observed above and below about 1240 ± 20° C.

Figure 3.3 shows representative x-ray scans in the four regions of temperature and current direction. During these scans, repeated observations of the laser diffraction patterns were made. For positive current, figure 3.3(b) and (d) represent the regions
associated with the frozen morphologies described in the previous section. At 1270°C, the x-ray scan shows the (1,0) facet peak while the laser diffraction pattern consisted of longitudinal spots. Both the x-ray and laser diffraction are indicative of surface faceting. The width of the (1,0) facet peak indicates an average facet size on the order of 1000Å. At 1200°C, the x-ray scan shows the step peak of a uniformly stepped phase while the laser diffraction pattern consisted of transverse spots as observed previously. The width of the step peak indicates a step correlation length on the order of 170Å.

For negative current, the x-ray and laser data indicate that the faceting instability is inverted in temperature meanwhile, the transverse instability is absent. Figure 3.3(a) and (c) represent two temperature regions for negative current. At 1275°C, the x-ray data shows a (1,0) facet peak while the laser observations also indicated faceting with longitudinal spots. The width of the x-ray peak indicates an average facet size on the order of 500Å. At 1270°C, the x-ray data shows a step peak consistent with a uniformly stepped phase. The width of the step peak indicates that the step correlation length is on the order of 300Å. Meanwhile, the laser observations indicated an optically ordered surface with only a specular reflection.

### 3.4 A Study of Flashing Instabilities

The dramatic results of the previous sections raise questions as to why previous studies consistently reported successful surface preparation by flashing regardless of the heating scheme. Therefore, a study of the effects of flashing on step order was decisively a prerequisite for studies of the low temperature instabilities. Here, a study of the effects of flashing a sample to various temperatures with positive and negative currents is presented. This study suggests that particular flashing conditions are preferred for sample preparation. This study also lead to the discovery of the step bunching instability above the 7 × 7 reconstruction for positive current.

The first flashings to be studied were performed at 1200°C for 1 minute in duration using positive current. Before removal of the oxide layer, the sample was annealed
Figure 3-4: Summary of High Temperature X-ray Profiles
at 900°C while the UHV chamber was baked to about 100°C. This produced broad (1,0) and bunched-step peaks. After flashing the sample several times, the facet peak disappeared and the step peak moved to the uniform density position. The step peak was broad indicating correlation lengths of (X and Y) in the longitudinal and transverse directions. Even through the peaks are broad, it is clear that on a time scale of minutes, there is a stabilizing force at 1200°C and positive current which will eliminate step bunching.

Surprisingly, the uniformly stepped surface was found to be unstable with respect to bunching at 900°C and positive current. Figure 3.4 shows x-ray scans taken within 10 minutes after flashing and about 2.5 hours after flashing. This instability occurs on a time scale of 10's of minutes.

The instability at 900°C, contradicts the reports of a stable uniformly stepped phase above the 7 x 7 reconstruction temperature. Therefore, this flashing study was repeated however, after cooling to 900°C, the current direction was immediately switched to negative current. Scans taken at 900°C within 10 minutes of flashing and about 1.5 hours after flashing are shown in figure 3.4. Comparing the scans in figure 3.4 (c) and (d) (the initial state) with the scans in figure 3.4(a) and (b) again clearly demonstrates the ordering in both the transverse and longitudinal directions due to the flashing. Furthermore, the scans in figure 3.4(c) and (d) show additional ordering after annealing for 1.5 hours at 900°C and negative current. This is consistent with the previous reports of a stable phase at this temperature. One must infer that previous studies either did not use direct current heating with current flowing in the positive (step-down) direction or were performed before the step bunching instability progressed.

Next, the effects of flashing to 1200°C with negative current was studied. Before flashing with negative current, additional step ordering occurred due to additional flashes with positive current and anneals at 900°C with negative current. The initial peak profiles are shown in figure 3.4 (a) and (b). As a result of the flashes with negative current, the steps ordered significantly. The scans taken after 3 flashes of one minute in duration are shown in figure 3.4 (c) and (d). The sharpening of the step
Figure 3-5: Step bunching at 900° C and positive current
Figure 3-6: Step ordering at $900^\circ$ C and negative current
peak indicates an ordering force on the time scale of minutes. The rapid sharpening of the step peak (on the order of minutes) suggests a greater stabilizing force with negative current than at positive current. These stabilizing forces are not completely consistent with the long time scale instabilities observed at 1200° C. Namely, with positive current, the surface is transversely unstable on long time scales while with negative current, the surface has a step bunching instability on long time scales.

In order to determine the effect of flashing as a function of temperature for both positive and negative current, a series of flashes at various temperatures were performed first with positive current then with negative current. Figure 3.4 shows scans taken at 900° C immediately after flashing with positive current before the instability at 900° C could develop. Up to about 1225° C, the steps became progressively more ordered with each flash. However, above 1225° C, the steps began to bunch during the 1 minute intervals of the flashing. In order to remove the step bunching, the sample was flashed to 1220° C between each consecutive higher temperature flash. The resulting step peaks were broadened by the prior step bunched state. The step bunching instability above 1225° C is consistent with the step bunching instability observed on long time scales.

The result of flashing at consecutively higher temperatures with negative current is shown in figure 3.4. These scans were taken at 900° C and negative current immediately after the flashes. The broad step peak shown in figure 3.4 is the result of first disordering the steps by the step bunching instability indicated in figure 3.4 (d) followed by flashing to 1220° C once at positive current followed by once at negative current. At 1260° C, the step ordering occurred rapidly during the flashes. Figure 3.4 (b) and (c) show the ordering after one flash and after three flashes of 1 minute duration at about 1260° C. The increased stabilizing force at 1260° C and above is consistent with stability observed on long time scale at these temperatures and negative current.

The greatest ordering was achieved by flashing above about 1250° C with negative current. Therefore, this is the preferred procedure for cleaning the surface and obtaining ordered steps.
Figure 3-7: Step ordering due to flashing at 1200° C with negative current
Figure 3-8: The effects of flashing at different temperatures with positive current
Figure 3-9: The effects of flashing at different temperatures with negative current
3.5 Low Temperature Current Effected Instabilities

Thus far, unambiguous data for the reconstruction driven step bunching has not been presented. For positive current, the three sets of behavior shown in figure 3.1 were observed depending on the sample preparation. After learning how to prepare a clean uniformly stepped surface, the 7×7 reconstruction/phase separation could be studied. A detailed discussion of our study is given in later chapters. However to complete this introduction, these instabilities are summarized with data obtained during our first study dedicated to them.

Representative x-ray scans are shown in figure 3.5 for four regions of temperature and current near \( T_c \). Figure 3.5(a) indicates a stable uniformly stepped phase above \( T_c \) for negative current. The sample surface was initially prepared in this state by flashing to 1275° C with negative current before studying a quenching-heating program for each current direction. For negative current, the scans taken after the sample was quenched to \( T_c - 75° C = 695° C \) are shown in figure 3.5(c). In this state, the sample faceted instantly due to the 7×7 reconstruction. The widths of the x-ray peaks indicate an average facet size on the order of 1800Å and a step correlation length on the order of 470Å. From the faceted state, the sample was heated slowly into the uniformly stepped phase. A scan taken after heating to \( T_c + 10° C = 880° C \) is shown in figure 3.5 (a) which shows first and second order diffraction peaks from the steps. The width of the first order step peak indicates a step correlation length of 6700Å.

For the second quenching-heating, the current direction was switched to positive followed by immediate quenching to 695° C. Again, the surface faceted instantly due to the 7×7 reconstruction. The scan in figure 3.5(d) indicates an average facet size of 1400Å and a step-correlation length of 410Å – slightly shorter lengths than for negative current. The sample was then slowly heated through \( T_c \). As \( T_c \) was approached, the step peak acquired a complicated structure apparently due to faceting at larger length scales. Figure 3.5(b) shows an x-ray scan taken 1° C above the temperature at which the 6/7 th’s peak disappeared. The facet peak width is
Figure 3-10: Summary of Low Temperature X-ray Profiles
approximately equal to the maximum longitudinal resolution and indicates an average facet size > 1.2 Å. The diffraction from the steps produced a rapidly changing multi-peaked structure as indicated in figure 3.5(b).

In addition to the longitudinal x-ray information given here, the transverse x-ray information is also interesting. The transverse information is provided with some of the more detailed studies in later chapters. In this introduction, the focus has been on giving an overview which will provide a context for the more detailed studies. Another aspect which has been lightly covered here is the time dependence of each observation. The time dependence is quite important in the study of instabilities therefore, time dependence is reported in the detailed studies which follow.
Chapter 4

A Theory of Step Flow with Electromigration

The Burton, Carera, and Frank (BCF) model of crystal growth is based on the terrace-step-kink (TSK) description of a surface. BCF analyzed the diffusion of adatoms on terraces with boundary conditions at the steps to predict the behavior of surfaces. Stoyanov applied the BCF model with an electromigrative term to vicinal surfaces to explain many aspects of the D.C. current induced instabilities on vicinal Si(111). In this chapter, we review the TSK description and the models of BCF and Stoyanov. Then we extend Stoyanov's model to incorporate the steric effects of step curvature. The steric effects can be used to explain the step rippling and step straightening for the step-up and step-down current directions respectively. Then in order to study the temperature dependence explicitly, we reformulate the model in terms of more fundamental physical parameters using the measured values of these parameters provided in the literature.

4.1 TSK and BCF Models

The terrace-step-kink (TSK) model is the starting point of many theories of equilibrium and non-equilibrium phenomena on surfaces. Atomic scale models of surface behavior may use a combination of statistical mechanics thermodynamics and kinetic
rate equations to model surface behavior. Statistical mechanics is generally applied to equilibrium behavior whereas kinetic rate equations are generally applied to dynamic behavior. On the other hand, thermodynamics can provide the basis of equilibrium models or provide steady-state parameters for kinetic rate equations.

The first atomic scale models to be developed were terrace-step-kink (TSK) models. In TSK models, the topography of a crystal surface oriented near to a high symmetry axis is described by a set of discrete jumps from one atomic plane to another. The discrete jumps are called steps while the flat regions are called terraces. In general, the steps are not straight but wander laterally along the surface. The step profile consists of discrete atomic sized translations called kinks. With terraces, steps and kinks defined, they can be assigned specific individual properties such as terrace, step and kink energies and aggregate properties such as step and kink densities. Furthermore dynamic processes can be defined such as the formation and annihilation of kinks, the movement of atoms from kink sites to the step edge sites or to terrace sites and from the surface sites to the fluid phase. These processes can proceed in the reverse direction as well.

BCF[5] used the TSK model to study growth on a surface vicinal to a high symmetry orientation. In the case that the exchange of adatoms directly between the kink sites and the vapor is negligible, the motion of the steps is governed by the exchange of atoms between the kink sites and the terraces sites and the terraces and the vapor phase and the kink sites. On the terraces, the adatom concentration obeys a diffusion equation with two source terms – one for evaporation and one for deposition. In this model, both evaporation and growth are realized. At the steps or at the kinks, the kinetics are treated as a perturbation of equilibrium. This allows boundary conditions to be written in terms of an equilibrium concentrations. Similarly, the kinetics between the terraces and vapor phase are formulated in terms of equilibrium concentrations. Using this formulation, expressions were found for the rate of flow of parallel steps, the nucleation rate and equilibrium shape of two-dimensional islands, and the growth structures near screw dislocations. This work was successful in predicting some phenomena qualitatively many years before they could be observed however,
quantitative agreement with experiments has yet to be achieved.

### 4.2 Stoyanov's Model of Current Induced Step Bunching

The stability of step flow is determined by the dynamic interactions between steps just as equilibrium faceting is determined by the static interactions between steps. The dynamic interactions between steps are mediated by the diffusion of adatoms on the terraces. Stoyanov has modeled the effect of a D.C. current on the stability of step flow by assuming that the adatoms on the terraces have a non-zero drift velocity, $V_a$, and by using BCF boundary conditions at the steps. The diffusion equation for a concentration of adatoms, $n$, can be written as

$$\frac{d^2 n}{dx^2} - \alpha^{-1} \frac{dn}{dx} - \lambda^{-2} n = 0$$  \hspace{1cm} (4.1)$$

where $\alpha = D_a/V_a$, and $\lambda = \sqrt{D_a \tau}$ is the diffusion length. $D_a$ is the diffusion coefficient of adatoms on the terraces while $\tau$ is the mean residence time of an adatom on the surface. The boundary conditions at the steps can be written as

$$\frac{dn}{dx} - \alpha^{-1} n = \epsilon^{-1} (n - n_e) \hspace{1cm} x = -l/2$$  \hspace{1cm} (4.2)$$

$$- \frac{dn}{dx} + \alpha^{-1} n = \epsilon^{-1} (n - n_e) \hspace{1cm} x = +l/2$$  \hspace{1cm} (4.3)$$

where $\epsilon$ is a step kinetic parameter with the dimensions of length and $n_e$ is the equilibrium concentration of adatoms.

By choosing the miscut direction to be toward the positive $x$ direction, boundary at $x = -l/2$ is at the lower side of a step while the boundary at $x = l/2$ is at the upper side of a step. A positive $V_a$ indicates an adatom drift velocity in the step-down direction as shown in figure 4.2. Since the right sides of equation's 4.2 and 4.3 are proportional to the net flow of atoms from the steps onto the upper and lower terraces, the velocity of a step, $V_{step}$, is given by
where

\[ n_e \phi(1) = n(-l/2) + n(l/2) \]  

\[ n_e \psi(l) = n(-l/2) - n(l/2) \]

and \( a \) is the surface lattice spacing. Equation 4.4 is derived for the case of a gradient in the step density, \( k_x = -l^{-2}l_x \), so that the terrace on the right of the step has a width of \( l + l_x/2 \) and the terrace on the left of the step has a width of \( l - l_x/2 \).

The stability of the step flow is found by calculating \( D_{step} \) according to equation 1.13

\[ D_{step} = l \frac{dV_{step}}{dl_x} = \frac{a^2 D_\alpha l^2 n_e}{2\epsilon} \frac{d}{dl} \psi(l). \]  

(4.7)

Stoyanov has discussed the analytical solution of equations 4.1 - 4.7 in various ranges of the parameter space. It turns out that \( \lambda \) and \( \alpha \) are the important parameters for
qualitatively predicting the regions of stability. \( n_e \) is proportional to the strength of the instabilities while \( D_a \) and \( \epsilon \) only cause shifts in the instabilities for physically reasonable ranges. A numerical solution for \(-D_{\text{step}}\) as a function of \( \lambda \) is given in figure 4.2(a) for \( V_a = 0.1a \text{ sec}^{-1} \) (solid line) and \( V_a = -0.1a \text{ sec}^{-1} \) (dotted line). For this solution, \( l = 50a \), and \( \epsilon = a\lambda/l \). The condition on \( \epsilon \sim O(a) \) implies negligible repulsive or attractive forces between the steps and the adatoms while the factor \( \lambda/l \) is used to roughly account for the temperature dependence of \( \epsilon \).

The regions in figure 4.2 where the lines are above zero (i.e. \( D_{\text{step}} < 0 \)) indicate step bunching instabilities. For \( V_a < 0 \), step bunching occurs for \( \lambda < \sim 2l \) whereas for \( V_a > 0 \), step bunching occurs for \( \lambda > \sim 2l \). Since \( \lambda \) is a decreasing function of temperature, this model implies that step bunching occurs at high temperatures for \( V_a < 0 \) and at low temperatures for \( V_a > 0 \). Comparing this with the phase diagram If the crossover corresponds to the inversion temperature near 1230° C in figure 1.2, then it follows that positive current corresponds to negative \( V_a \). This in turn implies that the effective charge of the adatoms is negative. On the other hand, if the crossover corresponds to the inversion temperature at 1025° C then one concludes that the effective charge of the adatoms is positive.

It is interesting to note that when step bunching occurs for \( \lambda > l \) with negative current, the step spacing in the low density regions, \( l_{\text{low}} \), should be stable at \( l_{\text{low}} \sim \lambda \). Therefore, \( c_{\text{low}} \neq 0 \). Meanwhile, the step density of the step bands \( c_{\text{band}} \rightarrow \infty \). On the other hand, when step bunching occurs for \( \lambda < l \) with positive current, the step spacing in the step bands, \( l_{\text{band}} \), should be stable at \( l_{\text{band}} \sim \lambda \). Meanwhile, \( c_{\text{low}} \rightarrow \infty \). The temperature dependence of the step spacings should be obtainable experimentally.

4.2.1 Analogy with Traffic Flow

It may be useful at this point to describe an analogy with traffic flow in order to help better understand the step bunching instabilities. During sublimation, the steps flow in the step-up direction. The stability of the step flow depends on the information exchanged between steps and the response to that information. A non-zero drift ve-
Figure 4-2: Numerical Solution to Stoyanov’s Model of Step Flow
locity of adatoms creates an imbalance in the flow of information between neighboring steps. For a drift velocity in the step-down direction, a step receives more information from the step ahead than from the step behind (assuming equal step separations). In traffic, this corresponds to drivers being focused on the car ahead. On the other hand, for a drift velocity in the step-up direction, a step receives more information from the step behind than from the step ahead. This corresponds to drivers being focused on the car behind. The effect of neighboring steps either ahead or behind a step is to increase the flow of adatoms to the step causing the step to slow down. The strength of this interaction depends on the distance between steps and the interaction distance. Since the steps interact via adatom diffusion, the interaction distance is of the order of the diffusion length.

Now consider a fixed average density of cars on a foggy highway where the thickness of the fog determines the distance over which the drivers are able to see neighboring cars. Thick fog corresponds to small diffusion lengths and high temperatures. For the case that drivers are focused on the car in front, the driver will slow down if s/he sees the car in front and drive at “normal” speed if s/he doesn’t. If the visibility is less than the average car spacing, most cars will be driving at normal speed and the flow of traffic is stable. On the other hand, if the visibility is greater than the average car spacing the cars behind will slow down at an exponential rate causing a non-linear instability in the car density (traffic jam). Note that the traffic jam occurs at conditions corresponding to low temperatures.

Now consider the case that drivers are focused on the car behind. The driver will slow down if s/he sees the car behind and drive at ”normal” speed if s/he doesn’t. If the visibility is less than the average car spacing most cars will initially be driving at normal speed, but the flow is unstable. The few drivers that can see the car behind them will slow down causing the cars to bunch-up behind them. At the same time, the separation between the cars ahead will increase creating vacant stretches of the highway. On the other hand, if the visibility is greater than the average car spacing, most drivers will be able to see the car behind them and they will simultaneously slow down to a stable, steady-state speed. In this case, the car bunching occurs at
conditions corresponding to high temperatures.

4.2.2 Crossover Temperature

In Stoyanov’s model, the instability crossover occurs at a temperature, \( T_c \), at which \( \lambda(T) = \xi l \). \( \lambda(T) \) can be estimated by using literature measurements of the surface kinetic parameters. The temperature dependence of the parameters in Stoyanov’s model can be determined by assuming kinetic forms for the rates of atomic processes\[11, 49\]. The diffusion coefficient and sublimation rate \( 1/\tau \) are given by

\[
D = a^2 \nu \exp\left[-(E_d/k_B T)\right] \tag{4.8}
\]

\[
1/\tau = \nu \exp\left[-(E_d/k_B T)\right] \tag{4.9}
\]

where \( \nu \) is an atomic frequency \((\sim 10^{13} - 10^{14})\), and \( E_d \) is the energy of diffusion and \( E_a \) is the energy of desorption. From equation 4.9, it follows that

\[
\lambda = a \exp\left[(E_a - E_d)/2k_B T\right]. \tag{4.10}
\]

Literature values commonly used for \( E_a - E_d \) are 0.8 ± 0.1 eV\[27, 2\]. Using this value, equation 4.10 yields \( \lambda = 17a \) to \( 37a \) (or 55Å to 121Å) at \( T = 1225^o \) C. This is consistent with the measured crossover temperature near \( 1225^o - 1250^o \) C on a 3° C.

4.2.3 Shortcomings of Stoyanov’s Model

Despite its success in predicting the current effected instabilities near a cross-over temperature, Stoyanov’s model has remained controversial due to several apparent discrepancies with experimental measurements. For example, Stoyanov’s model predicts that \( T_c \) should depend strongly on the step spacing, \( l \). This is in contradiction with the experiments of Homma et al.\[24, 23\] and others\[34, 44\] which found \( T_c = 1225 - 1250^o \) C on a range of \( l \) from 35Å to \( Y \). Furthermore, the REM experiments of Alfonso et al.\[2\] have indicated that the step velocity may be proportional to
the step spacing for temperatures up to 1300°C. Their data has been used to argue that λ < 1μ for temperatures up to 1300°C. However, this is in contradiction with previous literature measurements discussed above.

In addition, Stoyanov's model in its original form does not explain the crossover temperatures near 1350°C on an 8° miscut and near 1025°C on 1° to 4° miscut surfaces. Nor does it explain the straightening and wandering of the step profiles as a function of current direction. Several attempts have been made to extend Stoyanov's model or to apply different models to explain these phenomena. Pimpinelli et al[10] have investigated the possibility that an asymmetry in the rate of exchange of atoms between a step and the upper and lower terraces (Schwoebel effect) could be responsible for some of the step bunching instabilities. Their results suggest that the Schwoebel effects are small relative to the current effects. In another study[38] they consider the effects of advancies to explain the crossover temperature near 1350°C on small miscuts. Several studies have been made to explain either step straightening or step wandering instabilities by kinetic or Schwoebel effects during growth. However, to our knowledge, no previously published theory has succeeded to explain both step straightening and wandering as a function of current direction. Nor is there a published theory which explains the second crossover temperature near 1025°C on large miscuts.

4.3 Extensions of Stoyanov's Model

The transverse step wandering instabilities are not yet accounted for by this model. Here, an extension of Stoyanov's model is introduced which is qualitatively consistent with the observed step wandering instabilities. In order for there to be a transverse instability, the step velocity must vary along a step profile, \( V_{step} = V_{step}(y) \). If the \( x \) coordinate of the step profile is given by \( X(y) \) then it is plausible that the step velocity depends on \( y \) via the step curvature, \( w(y) \approx a\partial^2 X(y)/\partial y^2 \). In a perturbation analysis
of equations 4.1 through 4.3 one obtains

\[ V_{\text{step}} = V_0 + \delta w V_1 + \cdots (\delta > 0) \]  

(4.11)

where \( V_0 \) is the velocity for \( w = 0 \). Here, the criteria for an unstable step profile is that \( V_1 < 0 \). In order for a model to be consistent with experimental observations, \( V_1 \) must be positive for positive current and negative for negative current.

One possible perturbation, is to let \( n_e \) be a function of the step curvature and position on the terrace such that equations 4.2 and 4.3 become

\[ \frac{dn}{dx} - \alpha^{-1} n = \epsilon^{-1} (n - n_{e0} (1 - \delta w)) \quad x = -l/2 \]  

(4.12)

\[ - \frac{dn}{dx} + \alpha^{-1} n = \epsilon^{-1} (n - n_{e0} (1 + \delta w)) \quad x = +l/2 \]  

(4.13)

where \( n_{e0} \) is the equilibrium concentration for \( w = 0 \). The parameter \( \delta \) depends on the mechanism by which \( n_e \) is affected by the step curvature. The conjecture that \( n_e \) is not independent of the step profile is allowed by assuming that the step profiles are not in their equilibrium configuration. This is contrary to the BCF theory which uses a perturbation from equilibrium. Below it is shown that steric factors of step curvature produces \( \delta = 1 \).

The first two terms of the perturbation expansion \( n = n_0 + \delta w n_1 + \cdots \) are the exact solution of equation 4.1 with the modified boundary conditions in equations 4.12 and 4.13. It is easy to see that \( n_1 \) satisfies

\[ \frac{d^2 n_1}{dx^2} - \alpha^{-1} \frac{dn_1}{dx} - \lambda^{-2} n_1 = 0 \]  

(4.14)

with boundary conditions

\[ \frac{dn_1}{dx} - \alpha^{-1} n_1 = \epsilon^{-1} (n_1 + \delta w n_{e0}) \quad x = -l/2 \]  

(4.15)

\[ -\frac{dn_1}{dx} + \alpha^{-1} n_1 = \epsilon^{-1} (n_1 - \delta w n_{e0}) \quad x = +l/2 \]  

(4.16)
From equation 4.4 and 4.11 it follows that

$$\frac{eV_1}{a^2D_a\delta n_e} = \phi_1(l) + \frac{1}{2}H_z \frac{d}{dl}\psi_1(l) - 2$$  \hspace{1cm} (4.17)

where

$$n_e\phi_1(1) = n_1(-l/2) + n_1(l/2)$$  \hspace{1cm} (4.18)
$$n_e\psi_1(l) = n_1(-l/2) - n_1(l/2).$$  \hspace{1cm} (4.19)

Equations 4.14 through 4.19 were solved numerically by setting $\delta = 1$ and using the same parameters as before. Figure 4.2 (b) shows the ratio of $V_1$ to $V_0$ as a function of $\lambda$ for $V_a = 0.1a$ sec$^{-1}$ (solid line) and $V_a = -0.1a$ sec$^{-1}$ (dotted line). Since during sublimation $V_0 < 0$, the condition for instability is $V_1/V_0 > 0$. Figure 4.2 (b) shows that for $V_a > 0$, the step profiles are stable for all $\lambda$ and for $V_a < 0$, the step profiles are unstable for all $\lambda$. Experimentally, wavy steps are observed for positive current. Therefore, this model of the step wandering instability suggests that the effective charge of the adatoms is negative which is consistent with the requirements of the step bunching instabilities.

### 4.4 Temperature Dependence

In order to obtain the temperature dependence of the instabilities i.e. $-D_{step}$ and $V_1/V_0$, it is necessary to determine the temperature dependences of $\lambda$, $D_a$, $V_a$, $n_e$, and $e^{-1}$. The temperature dependences of $D_a$ and $\lambda$ have already been given in equations 4.8 and 4.10. The drift velocity is given by

$$V_a = D_a f / k_B T$$  \hspace{1cm} (4.20)

where $f$ is the force on the adatoms due to the electric field, $E_{el}$, i.e. $f = q^* E_{el}$ where $q^*$ is the effective charge of the adatoms. In general, $q^*$ can be positive or negative depending on the degree of ionization $q_o$ and the interaction with the positive and
negative charge carriers. In other words, $q^* = q_o + q_{wind}$.

The temperature dependences of the remaining parameters $n_e$ and $\epsilon^{-1}$ are obtained by considering the kinetics at the step edges. Figure 4.4 (a) shows the energy barriers for the various motions of atoms on the surface. At equilibrium, the rates of atom dis-association from a step are equal to the rates of adatom attachment, for the lower terrace $r_1 = r_2$ and for the upper terrace $r_3 = r_4$. In terms of kinetic parameters, these rates can be written as

$$r_1 = r_3 = (\nu/a)\exp\left[-(E_r + E_d + E_n)/k_BT\right]$$

$$r_2 = r_4 = a\nu\exp\left[-(E_r + E_n)/k_BT\right]n_e.$$

From this it follows that

$$n_e = \exp\left[-E_n/k_BT\right]/a^2.$$  \hspace{1cm} (4.23)

From equations 4.2 and 4.3, it is easy to show that $r_1 = D_\epsilon\epsilon^{-1}n_e$. Therefore,

$$\epsilon = \exp\left[-E_r/k_BT\right]/a$$  \hspace{1cm} (4.24)

Some measurements of these activation energies have been reported in the literature. The most commonly quoted values are $E_n + E_d = 2.2 \pm 0.1$ eV, $E_d = 1.1$ eV, and $E_a - E_d = 0.8 \pm 0.1$ eV. On the other hand, values for $E_r$ have not been reported to our knowledge. However, one caveat is that these measurements are open to interpretation and may include contributions from $E_r$.

Using the above relations, $-D_{step}$ and $V_1/V_0$ can be solved numerically. For the calculations described here, parameters were selected to be $E_a = 1.9$ eV, $E_n = 1.1$ eV, $E_d = 1.1$ eV, $\nu = 3 \times 10^{13}$ sec$^{-1}$, and $a = 3.28 \text{Å}$. Figure 4.4 (a) shows the step bunching instability for negative current and $E_r = 0$ for $l = 50 \text{Å}$, 60Å, and 80Å. Figure 4.4 (b) shows the step bunching instability for $l = 60 \text{Å}$ and $E_r = 0$ eV and ±0.05 eV. Note that the crossover temperature is a strong function of both $l$ and $E_r$.

The effects of curvature can also be investigated numerically. Figure 4.4 (a) shows
Figure 4-3: The Kinetics at a Step
Figure 4-4: Step Bunching for Various Step Spacings and Step Potentials
the step bunching instabilities as a function of temperature, current direction, and step curvature for \( l = 60 \text{Å} \) and \( E_r = 0 \). \( w = 0 \), corresponds to Stoyanov's model.

In this case, a single crossover temperature is observed near 1200° C. The results are also shown for \( w = \pm 1 \times 10^{-5} \) with \( \delta = 1 \). These results suggest that step curvature can modify the step bunching instabilities.

Figure 4.4 (b) shows the transverse step instability for positive and negative current. Transverse waves are predicted for positive current whereas straightened steps are predicted for negative current. For this reason, the effects of step curvature on the step bunching instabilities are most likely to occur with positive current. Figure 4.4 shows the step bunching instabilities as a function of curvature for positive and negative current at 900° C and 1100° C. For positive current at 900° C, step bunching occurs for large positive step curvature. A similar conclusion follows at 1100° C. However, experiments show that step bunching occurs at 900° C, but not at 1100° C. In order for this model to be consistent with experimental observations, it must be true that the step curvature is much less at 1100° C than at 900° C. The smaller length-scale morphology observed at lower temperatures would tend to support this hypothesis. The dominant transverse modes are selected by non-linear effects which are not contained in this theory.

### 4.5 The Steric Effects of Step Curvature

The steric effects of step curvature produce a small inequality between the steady-state concentrations on the lower terrace \( n_e^- \) and on the upper terrace \( n_e^+ \). This can be seen by considering a circular island as shown in figure 4.4 (b). The total flow of atoms to and from the step is given by

\[
2\pi R r_1 = 2\pi (R + a)r_2 \\
+ \quad = \quad - \\
2\pi R r_3 = 2\pi (R - a)r_4
\]

(4.25)  
(4.26)  
(4.27)
Figure 4-5: Step Instabilities as a Function of Temperature
Figure 4-6: Step Bunching as a Function of Step Curvature
From this it follows that

\[ n_e^- \approx n_{eo}(1 - w) \quad (4.28) \]

and

\[ n_e^+ \approx n_{eo}(1 + w) \quad (4.29) \]

where \( w = a/R \) is the step curvature.
Chapter 5

Optical Microscopy and AFM

Over the course of our studies, we have observed a great variety of mesoscopic features on surfaces miscut $3^\circ$ toward the $\langle 11\bar{2} \rangle$ direction using real-space imaging techniques. The development of these features is caused by the underlying instabilities of the step flow during sublimation. In this chapter, we present images which illustrate the general patterns in the phenomenology. In addition to step bunching (longitudinal) instabilities, there also exists step wandering (transverse) instabilities at mesoscopic length scales. Many published images of vicinal Si(111) surfaces indicate mesoscopic transverse fluctuations of the surface similar to those presented in this chapter. However to our knowledge, these features have not been studied in detail.

Our samples were cut from p-doped Si wafers which were polished on both sides. Since the front and back sides of the sample are parallel, they have the same average step density. However, for a given current running through the sample, the current polarity with respect to the step inclination is opposite for the opposite sides of the samples. Therefore, both current polarities can be studied on a single sample with a single current. Samples were heated in UHV to various temperatures for various lengths of time. The mesoscopic surface morphologies that developed at sublimation temperatures were easily preserved by quenching the samples to room temperature. Since the surface morphologies are stable in atmosphere, several imaging techniques can be applied conveniently. In this paper, the results of optical microscopy (OM)
and atomic force microscopy (AFM) studies of several samples are reported. All OM images presented here are arranged such that the $<11\bar{2}>$ direction is toward the top of the page. The microscope magnification was set at 50× for these photographs. The OM photographs presented here were cropped to reveal $148\mu \times 112\mu$ of surface area. On the other hand, the AFM images correspond to $50\mu \times 50\mu$ of surface area.

5.1 Surface Morphologies Near $1225^\circ$ C

In order to study the late-stage instabilities near $1225^\circ$ C, a sample (sample 9-94) was annealed for 1.5 hours at about $1224^\circ$ C. Previous to this a uniform stepped phase was observed on one side of the sample. The uniform stepped phase was obtained by flashing many times above $1250^\circ$ C with negative current. During this high temperature treatment, it is expected that the backside of the sample with positive current underwent step bunching. The x-ray study indicated that the sample temperature variation across the width of the sample near the center was less than $2^\circ$ C at the $7 \times 7$ reconstruction temperature ($\sim 870^\circ$ C). However at higher temperatures, the increased rates of radiation losses caused the regions near the edges of the sample to be cooler than regions further from the edges.

Figure 5.1 shows the late-stage morphologies for both positive and negative current directions along a gradient in the annealing temperature. The photographs (a)-(c) were taken of the side of the sample with negative current while the photographs (d)-(f) were taken of the side of the sample with positive current. The top photographs (a) and (d) were taken of the relatively hotter regions while the bottom photographs (c) and (f) were taken of the relatively cooler regions. The various images of the surface indicate a continuous change in morphology as a function of annealing temperature for both current directions.

5.1.1 Negative Current

The series of photographs in figure 5.1(a)-(c) show different stages of faceting across the width of the sample for the surface exposed to negative current. Of the three
Figure 5-1: Photographs of Morphologies for Two Current Directions
photographs, the top one shows a region furthest from the edge of the sample while the bottom one shows a region nearest to the edge of the sample. In these photographs, the darker regions highlight the step bands. The top photograph shows little contrast while the middle photograph shows greater contrast while the bottom photograph shows the greatest contrast. The increase in contrast suggests an increasing step bunching amplitude toward the edge of the sample. The density of the step bands indicates that their average separations $L_{\text{band}}$, are $4.6\mu$ for the top photograph, $4.0\mu$ for the middle photograph, and $4.2\mu$ for the bottom photograph. The average step band widths, $W_{\text{band}}$, are $2.3\mu$ for the top photograph and $2.0\mu$ for the middle photograph and $1.4\mu$ for the bottom photograph. This indicates that the $L_{\text{band}}$ is nearly constant with increasing amplitude whereas $W_{\text{band}}$ decreases (and $c_{\text{band}}$ increases) with increasing amplitude.

Other samples have shown that step bands with separations as large a $20\mu$ terminate abruptly along a temperature gradient. Therefore, with additional annealing one would expect the step bands in the photographs in figure 5.1(a)-(c) to undergo additional coarsening. In this case, it is consistent to view the differences in the three photographs as being due to different stages of faceting rather than due to a temperature gradient.

The photographs in figure 5.1(a)-(c) also indicate a mechanism for coarsening. The dark bands are seen to split and join at many locations. These locations can be considered to be defects in the step bands. In the middle photograph, these defects are arranged mostly along domain walls. This suggests that coherent fluctuations nucleate in domains which then spread until they meet the coherent fluctuations of neighboring domains. The domain size in the middle photograph is about $40\mu$ in diameter. As the step bunching amplitude increases, the band defects become mobile and disordered. This can be seen in the bottom photograph where the domain walls have disappeared. Presumably, coarsening occurs as the motion of defects redistribute the steps among the step bands. An alternate mechanism of coarsening may occur by some step bands slowly disintegrating as the steps move across the low step density regions. The images due not rule out this possibility entirely.
Several additional observations can be made about the step bunching process. While there is little variation of the step band spacing over the sample, there is a large variation in step bunching amplitude. This would suggest that step bunching initiates at a mesoscopic wavelength. This in turn suggests that the step bunching occurs as a cooperative effect over many step spacings. If this cooperation is mediated by diffusion (as opposed to stress or dipole interactions), then it follows that the diffusion length is greater than the step spacing, $\lambda > l$. The absence of step bunching at high temperatures may indicate that the diffusion length has decreased to satisfy $\lambda < l$. This argument suggests that the initial facting wavelength should depend on the sample temperature.

5.1.2 Positive Current

Photographs (d)-(f) show the evolution of the late-stage morphologies with temperature for positive current. Figure 5.1(d) and (e) show the late-stage step bunching instability. The step bunches appear as dark bands while the low step density regions ((111) facets) appear as bright bands. The average width of the step bands in figure 5.1 (c) is 3.6$\mu$ while the average spacing between step bands is 11$\mu$. On the other hand, the average width of the step bands in figure 5.1 (d) is 6.2$\mu$ while the average spacing between step bands is 10$\mu$. This shows that the width of the step bands relative to the width of the (111) facets decreases with increasing temperature. Figure 5.1(f) shows the late stage morphologies for a region of the sample which was heated below the step bunching instability. In this image, the (111) facets are essentially absent causing the step bands to be joined together.

These photographs also show a transverse instability in the step profile. The average wavelength of the transverse fluctuations is about 12$\mu$, 9$\mu$, and 8$\mu$ for photographs (d), (e), and (f) respectively. The variation in the band thicknesses are relatively small compared with the amplitude of the band wandering. This implies that the atomic steps wander coherently within the step bands at the $\sim 8 - 12\mu$ length scale. There is also some coherence between the transverse fluctuations of different step bands. The resulting coherence length of the mesoscopic step wandering
is largely a function of temperature. As the temperature decreases, the coherence length increases. Although the inter-band coherence is relatively weak in figure 5.1 (d), the coherence is much stronger as the relative width of the (111) facets decrease as in figure 5.1 (e). In the absence of step bands, the interband coherence is much greater as shown in figure 5.1 (f).

5.2 Defects and Step Bunching Wavelengths

The hypotheses that step bunching with negative current is a cooperative effect and that the step bunching wavelength should vary with temperature are supported by images from another sample (sample 2-94). This sample is identical to the one used in the x-ray study of flashing described previously. Near the end of the x-ray study, a very well-ordered step phase was observed. Just before quenching the sample to room temperature, the sample was annealed at 1260° C for 20 minutes and then at 1240° C for 20 minutes with negative current. Due to temperature gradients, step bunching was observed away from the center of the sample. Figure 5.2 shows a sequence of photographs taken along a temperature gradient where photograph 5.2 (a) was taken of a hotter region while photograph 5.2 (d) was taken of a cooler region.

Photograph 5.2 (a) shows a low amplitude fluctuation except in a region near a defect which shows a large amplitude fluctuation. The large amplitude fluctuations around the defect are interesting because they extend beyond a few wavelengths around the defect. Images of many defects showing similar phenomena highly suggests that the step bunching is a cooperative effect. This also means that a small concentration of defects may cause the entire surface to be unstable. If for example C impurities can cause step bunching then one might observe step bunching below the desorption temperature of C (~ 1250° C).

Figure 5.2 (b) and 5.2 (d) show photographs of regions with nearly constant step bunching wavelengths of 2.5μ and 3.6μ respectively. On the other hand, figure 5.2 shows a photograph of a transition region between two step bunching wavelengths. By assuming that the temperature gradient across the transition region is small compared
Figure 5-2: Photographs of Morphologies for Negative Current
to the \( \sim 20^\circ \) C drop in temperature during the annealing cycle, one can conclude that the step bunching in figure 5.2 (b) was nucleated at about \( 20^\circ \) C lower than the step bunching in figure 5.2 (d). This suggests that the step bunching wavelength is a decreasing function of temperature (similar to the dependence of phase separation wavelengths on temperature). Furthermore, it is interesting that step bunching did not occur in the region of figure 5.2 (b) during the higher temperature anneal even though its temperature was below the crossover temperature (being nearly the same as that of the region of 5.2 (d) which did undergo step bunching). This suggests a metastability phenomena.

In most discussions of the current induced instabilities, the concept of metastability has been ignored. The model of surface stability presented in an earlier chapter is valid for small fluctuations from a highly ordered initial state. Consider the case where the steps on a surface contain large fluctuations. The fluctuations may cause an instability to develop without regard to the average step spacing. This may explain the fact that the measured cross-over temperatures are independent of the average step spacing.

### 5.3 Saturated Surface Morphologies

The photographs in figure 5.3 show the surface of a sample (sample 9-93) which was annealed for about 70 hours at \( 1130^\circ \) C. This sample happened to have a very uniform temperature profile. In photograph 5.3 (a), the step bands are indicated by the brighter regions while the low step density regions are indicated by the medium grayscale regions. The reversed brightness scale is due to a change in the relative position of the illuminating light source.

In figure 5.3 (a), the average width of the step bands is about \( 2.2 \pm 0.2 \mu \) while the average spacing between step bands is about \( 14 \mu \). The straightness of the step bands is almost as surprising as the step band wandering for the opposite current polarity. The low degree of transverse fluctuations of the step bands creates low step density regions of very large extent in the \( < 1\bar{1}0 > \) direction. The the low step density
Figure 5-3: Photographs of Step Bands and Step Ripples formed at 1130° C
regions often extend across the entire width of the sample (\( \sim 8 \text{ mm} \)). Other surfaces annealed with this current direction have shown both larger and smaller average spacings between step bands. The forks in the step bands visible near the bottom of the photograph in figure 5.3 further indicate a coarsening mechanism. Also, one may notice that some of the low step density regions exhibit finger-shaped contrast. The structures have an average transverse wavelength of 7.5\( \mu \). Due to the difficulty in interpreting the surface profile from optical contrast, the morphology of these features will be discussed in conjunction with AFM plots below. However, here we note that the relative uniformity of their widths and spacings.

The photograph in figure 5.3(b) shows the side of sample 9-93 which was heated with positive current. The transverse fluctuations have an average wavelength of 7.5\( \mu \). In this photograph, the coherence of the step wandering is much greater than in figure 5.1 (f). One measure of the coherence is the distance over which a crest of the fluctuations can be followed vertically in an image. One can see that in photograph 5.3(b), it is much easier to follow a crest vertically across the entire image than is for photograph 5.1(f). The average distance between forks in the crests is about 120\( \mu \).

### 5.4 Positive and Negative Step Bands

Interesting morphological structures were observed on a sample (sample 3-94) which had been alternately heated many times between 1050\(^\circ\) C and 1260\(^\circ\) C with negative current and to 1300\(^\circ\) C with positive current. Step bunching instabilities occur for most of these conditions. Two photographs from this sample are shown in figure 5.4. The top photographs shows a hotter region of the sample along a temperature gradient than the bottom photograph. The heating history of this sample is too complex to separate the causes of the various features observed. Even so, these features provide some insight into the relationship between the finger-like features observed in the low step density regions for negative current and the transverse step wandering for positive current.

The photograph in 5.4 (a) shows two types of step bands. The bright regions
Figure 5-4: Positive and Negative Step Bands
indicate step bands with an inclination toward the miscut direction (positive steps) whereas the dark regions indicate step bands with an inclination in the opposite direction (negative steps). The existence of positive and negative steps increases the total number of steps. Therefore, the total number of steps is not always conserved at high temperatures. The positive step bands are straight whereas the negative step bands wander. Since the negative step bands are exposed to opposite current direction relative to their inclination compared with positive step bands, the simultaneous observation of two instability conditions is possible when the total number of steps is not conserved.

Some of the negative step bands in figure 5.4 resemble the finger-like structures observed in figure 5.3 (a). This resemblance is especially clear in the bottom photograph in figure 5.4 where the negative step bands have formed highly correlated finger-like structures. Similar highly ordered finger-like structures have been observed on surfaces which were annealed for many hours with negative current without switching current directions.

The appearance of negative steps is an indication that Lockheime nucleation may be occurring. However, it is clear from figures 5.1 and 5.4 that the negative steps are produced near the lower edge of the step bands. In this case, the actual mechanism of negative step formation may be different from that of Lockheime nucleation.

5.5 AFM Images

As mentioned above, the surface profile is difficult to obtain by optical contrast alone. Therefore, it is useful to use AFM to study the surface profiles. AFM was used to measure the surface height on a grid of 256 x 256 points covering 50µ x 50µ of the surface area. Figures 5.5 and 5.5 show 3-dimensional plots of the surface profiles of sample 9-93 which was heated to 1130° C with negative and positive current respectively. Figure 5.5 shows the profile of the first AFM scan from figures 5.5 and 5.5. Analysis of the profile for negative current indicates that the average step band spacing is about 16µ and that the step bands are inclined by about 25 – 30° from the
(111) facets.

The \( \sim (111) \) regions are mostly flat except near their lower boundaries whereas the step bands are curved. The curvature of the profile near the boundaries indicates that capillary forces are balancing the effects of the surface stress created at the boundaries. The lower ends of the \( \sim (111) \) facets have a downward curvature indicating the presence of negative steps. In figure 5.5, there are a few instances of the finger-like structures observed in the photographs. The profiles confirm that these structures are depressions formed by negative steps. This is consistent with the previous interpretation of the photographs.

Figure 5.5 shows the profile of a surface subjected to positive current. The surface profile is smooth with no sharp edges. The transverse fluctuations appear sinusoidal with a slowly varying phase and amplitude. The average amplitude is about 0.3\( -0.4 \mu \). The sinusoidal nature of the profile would suggest that the fluctuations are due to dynamic effects rather than surface energy effects. A numerical study of a transition from thermal fluctuations to chaotic fluctuations on surfaces have yielded surfaces profiles of surprising likeness to those of figure 5.5.

This work made use of MRSEC Shared Facilities supported by the National Science Foundation under Award Number DMR-900334.
Figure 5-5: AFM Profile of Step Bands for Negative Current
Figure 5-6: AFM Profile of Step Wandering for Positive Current
Figure 5-7: Single AFM Scans
Chapter 6

A Laser Study

The images in the previous chapter show that optical studies can be very useful in studying the current effected instabilities. While the imaging studies provide detailed knowledge of the surface profiles, they are not easily performed in situ. Therefore, in situ measurements are more conveniently made using diffraction techniques. In this chapter, we report on the application of laser diffraction to the current effected instabilities. The shapes of the laser diffraction profiles depend on the degree of coherence in the surface morphology. Coherent fluctuations create multiple diffraction peaks whereas incoherent fluctuations create a specular reflection distribution which indicates the distribution of surface normals just as in x-ray diffraction. The intensity profile perpendicular to the surface (out-of-plane) provides information about the shape of the surface profile. The intensity of the specular intensity is used to measure the growth of the fluctuation amplitude in situ. The growth rate as a function of temperature indicates an energy of $2.7 \pm 0.1$ eV.

6.1 Experiment

Vicinal Si(111) samples miscut $3^\circ$ toward the $<11\bar{2}>$ and $<\bar{1}12>$ directions were cut to about 30 mm in length in the direction perpendicular to the steps and about 8 mm in width. The samples were prepared in our UHV optical chamber equipped with an 8" viewport. A double-axis rotary feedthrough and a gearbox provided the
usual $\chi$ and $\phi$ rotations of 4-circle diffraction geometry. The samples were mounted so that the rotational axes were near the surface plane with the $\phi$ axis parallel to the steps. With this configuration, the sample normal can be aligned with the momentum transfer to measure specular reflectivity. Alternatively, by moving $\chi$ and $\phi$ angles, the momentum transfer may obtain surface-plane components. The pressure in the UHV chamber remained below $5 \times 10^{-9}$ torr during data collection.

A 2 mW Helium-Neon polarized alignment laser with a $0.2^\circ$ beam divergence was directed toward the sample through the viewport. Attenuators were used to adjust the incident intensity. A photodiode detector was used to monitor the reflected laser light intensity through the viewport. A square aperture was used to set the detector resolution at $0.2^\circ$ by $0.2^\circ$ during two-dimensional scans while for one-dimensional scans the resolution was decreased to about $3^\circ$ in the direction perpendicular to the scans. A focusing lens, a laser-line interference filter, and a second aperture at the focal point were used to select the sample image to be roughly equal to the illuminated spot size (about 1mm radius). The incoming and outgoing paths were $3^\circ$ apart and fixed. A beam splitter was used to monitor the laser power output.

6.2 Scans Parallel to the the Surface

6.2.1 Sample 11-93

Figure 6-1(a) through (d) show contour plots of the reflected light intensity projected onto the surface plane from samples heated to different temperatures with different current directions. These samples will be referred to as samples (a) through (d) respectively.

Samples (b) and (c) are miscut $3^\circ$ toward $< \overline{112} >$. Physically they are the same sample (sample 11-93) studied at different times. After degassing below 1000°C, the sample was heated to 1190°C with negative current. One-dimensional scans of the laser diffraction profiles are shown in figure 6-2(a)-(c) for three different times. Initially while the specular peak decreased, multiple order peaks formed with spacing
Figure 6-1: Contours of Laser Diffraction Profiles
\[ \Delta k_L = 1.4 \mu^{-1} \] corresponding to a wavelength of 4.5\( \mu \). As the specular peak disappeared, the multiple order peaks were being replaced by a facet peak near \(-1.0 \mu^{-1}\) corresponding to an average orientation of about 3° from the surface normal, and a step peak near 3.0\( \mu^{-1} \) corresponding to an average orientation of about 9° from the surface normal. This condition is shown from 3 until 5 hours after heating in figure 6-1(c). Both the facet peak and step peak are sharp in the transverse direction and broad in the longitudinal direction. Assuming a triangular hill-and-valley surface profile and assigning the length of each segment to be \( \sim \sigma_L^{-1} \), the average surface orientation is calculated to be tilted 2.3° toward the \( <11\bar{2}> \) direction which is in reasonable agreement with the measured tilt of 2.8°.

Figure 6-3 shows the transverse profile of the step peak in (a) and the longitudinal profile of both peaks in (b). The data in 6-3 (b) were obtained by taking the \( k_T = 0 \) slice of the two-dimensional scan of figure 6-1(c). Similarly, the data in 6-3 (a) were obtained by taking the \( k_L = 3.0 \) slice of the two-dimensional data in figure 6-1(c). The transverse profile was fit to a Lorenzian power lineshape while the longitudinal profile was fit to the sum of a Lorenzian power at the facet peak position and a Gaussian component at the step peak position. The fits are shown as solid lines in figure 6-3 and the fit parameters are given in table 6.1.

After the faceting instability had saturated, the temperature was cycled many times above 1250°C over a period of several days. Above about 1250°C, a bright specular peak and diffuse peak were observed similar to that in figure 6-1(a). At 1230°C, the current direction was reversed and transverse peaks appeared similar to those in figure 6-1(d). Then after heating the sample above 1250°C for many hours, the data represented in figure 6-1(b) were taken. However, the thinning of the sample due to sublimation caused severe temperature gradients and difficult temperature control. Therefore, the quality of the data in figure 6-1(b) is questionable.

### 6.2.2 Sample 8-93

Samples (a) and (d) are miscut 3° toward \( <1\bar{1}2> \). Physically they are the same sample (sample 8-93) studied at different times. After degassing below 1000°C, the
Figure 6-2: The time dependence of laser diffraction profiles.
Figure 6-3: Laser Diffraction Profiles for Sample (c)
### Table 6.1: The peak positions and peak widths for the laser diffraction profile of samples (a) and (c)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak</td>
<td>Sharp SR</td>
<td>Broad SR</td>
</tr>
<tr>
<td>$k_T$ ($\mu^{-1}$)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$k_L$ ($\mu^{-1}$)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\sigma_T$ ($\mu^{-1}$)</td>
<td>$0.015 \pm 0.001$</td>
<td>$0.044 \pm 0.001$</td>
</tr>
<tr>
<td>$\sigma_L$ ($\mu^{-1}$)</td>
<td>$0.0062 \pm 0.0005$</td>
<td>$0.051 \pm 0.001$</td>
</tr>
<tr>
<td>$\eta_T$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta_L$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 6.2: The peak positions and peak widths for the laser diffraction profile of sample (d)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order</td>
<td>$k_T$ ($\mu^{-1}$)</td>
</tr>
<tr>
<td>-3</td>
<td>$-2.77 \pm 0.4$</td>
</tr>
<tr>
<td>-2</td>
<td>$-1.85 \pm 0.01$</td>
</tr>
<tr>
<td>-1</td>
<td>$-1.000 \pm 0.004$</td>
</tr>
<tr>
<td>0</td>
<td>$0 \pm 0.01$</td>
</tr>
<tr>
<td>1</td>
<td>$0.984 \pm 0.004$</td>
</tr>
<tr>
<td>2</td>
<td>$1.87 \pm 0.01$</td>
</tr>
<tr>
<td>3</td>
<td>$2.75 \pm 0.04$</td>
</tr>
</tbody>
</table>
sample was heated to 1190°C with positive current. The time dependence of the laser diffraction profiles was similar to that illustrated by the one-dimensional scans in figure 6-2(d)-(f) for sample 9-93 (not sample 8-93) which was heated to 1130°C with positive current. Initially, only a bright specular peak was present. As the specular peak decreased, first order peaks \( (n = \pm 1) \) appeared in the transverse direction. The first order peaks occur at \( k_{\pm 1} = \pm 0.99\mu^{-1} \) indicating a surface height fluctuation with wavelength of about 6.3μ. Later, higher order peaks and a second broader peak around the specular position appeared. After 4 hours, the data represented in figure 6-1(d) were collected over a period of 2 hours. The peaks moved inward slightly with time as is evident by the tilt in the peak contours in figure 6-2(d).

For sample (d), figure 6.2.2 shows the transverse profile in (a) and the longitudinal profile of several peaks in (b). The data in 6-3 (a) were obtained by taking the \( k_L = 0 \) slice of the two-dimensional scan of figure 6-1 (d). The data in 6.2.2 (b) were obtained by taking the \( k_T = k_n \) slice of the two-dimensional scan of figure 6-1(d) where \( k_n \) is the \( n \)th order peak position in figure 6.2.2 (a). The longitudinal profiles were then offset in the transverse direction by \( k_n \) so that they can be easily identified in the figure.

In order to find the peak widths and intensities, the scattering profiles in figure 6.2.2 were fit to a sum of Gaussians in an iterative process. First the transverse profile was fit with one Gaussian component at each peak position and a very broad Gaussian background. The resulting series of widths, \( \sigma_T \) are given in table 6.2 and are plotted in figure 6.2.2 a. Next, the longitudinal profiles were fit with one Gaussian component per peak. The fits are shown as dashed lines in figure 6.2.2 and the widths, \( \sigma^{(1)}_L \), are given in table 6.2 and are plotted in figure 6.2.2 (a). Note that the peak widths are isotropic which is not true for step bunching.

The fits in figure 6.2.2 (b) indicate that a single Gaussian component is not sufficient to describe the profile shape. Better fits are obtained by using two Gaussian components per peak. In addition, a broad Gaussian component was used at \( K_L > 0, K_T = 0 \). The resulting fits are shown as solid lines in figure 6.2.2 (b). The fit widths, \( \sigma^{(1)}_L \) and \( \sigma^{(1)}_T \), are shown in table 6.2 and are plotted in figure 6.2.2 (b).
Figure 6-4: Laser Diffraction Profiles for Sample (d)
Figure 6-5: Peak Widths for Sample (d)
Since the diffraction peaks appear isotropic, the transverse profile can be fit to two Gaussian components per peak by fixing the transverse widths to be identical to the longitudinal widths. The resulting fit is shown in figure 6.2.2 (a) by a solid line. The two dashed lines show the contribution of the different sets of Gaussians in the fit. It is interesting that the \( \sigma_n^{(i)} \) appear to satisfy the relations

\[
\begin{align*}
\sigma_n^{(1)} &= |n| \sigma_1^{(1)} \\
\sigma_n^{(2)} &= (|n| + 2^{1/2}) \sigma_1^{(1)}.
\end{align*}
\]

In equation 6.2, the \( n = 0 \) widths are promoted to the next series and the sharp specular spot which is almost gone in these profiles is put in the first series.

The dominant effect of the modulation is to create phase shifts in the reflected amplitude. For a coherent incident beam, the reflected intensity is given by

\[
I(k) \sim \int \langle e^{i k_s (h(r) - h(0))} \rangle e^{i k_s \cdot r} dr
\]

where \( r \) and \( k_s \) span the sample surface. This expression can be rewritten in terms of the \( k_s \)-space moments of the surface in the \( z \)-direction,

\[
I(k) \sim 2\pi \delta(k_s) + \sum_{n>0} (i k_s)^{2n} M^{(2n)}(k_s)/(2n)!
\]

\[
M^{(2)}(k_s) = \int \langle [h(r) - h(0)]^2 \rangle e^{i k_s \cdot r} dr
\]

\[
M^{(2n)}(k_s) = \left( M^{(2)}(k_s) \otimes \cdots \otimes M^{(2)}(k_s) \right)
\]

where the \( \otimes \) operator denote a convolution operation.

Now consider surface fluctuations with a Gaussian distribution of wavelengths, \( \rho(q) \sim \exp[-(q - q_0)^2/2\sigma_q] \). If broad range of \( q_l \) occur within the surface coherence distance, then the convolutions in equation 6.6 can increase the observed peak widths by \( 2^{1/2}\sigma_1 \). On the other hand, if the distribution of \( q_l \) is integrated outside the surface coherence distance, then the observed peak widths vary as \( \sim |n| \). Therefore, the
relative amplitudes of the two series of Gaussian components used to fit the profiles in figure 6.2.2 indicate that the surface coherence distance is not very large.

After 10 hours, the step wandering instability had begun to saturate. Therefore, the current direction was reversed to negative current. This caused the features in the transverse direction to disappear slowly and new features to develop in the longitudinal direction. After 7 hours at negative current, the sample was heated to 1295°C causing the longitudinal features to move gradually inward until only a sharp specular spot and a weaker broad peak surrounding the specular position were present.

A two-dimensional scan taken after cooling to 1265°C is represented in 6-1(a). The sharp specular spot is 100 times brighter than the broader component and is narrower than the inner most contour in figure 6-1 (a). Figure 6.2.2 shows the transverse and longitudinal profiles obtained by taking slices from the two-dimensional scan. The profiles were fit to a sharp Gaussian peak convolved with the square resolution and a broader Gaussian component. The fits are shown as solid lines in figure 6.2.2 and the peaks widths are shown in table 6.1. Since the sharp specular peak is saturated in this profiles, the widths of the sharp specular peak were obtained from other scans with a lower laser intensity.

Since the intensity of the specular peak is much greater the the intensity of the broader peak, it is reasonable to consider only the first two terms in equation 6.3. They can be rewritten as

\[
I(k) \sim N\delta(k_x) + (k_z)^2 \int \langle h(r) h(0) \rangle e^{ik_r r} dr. \tag{6.7}
\]

The specular peak arises from the first term while the broader peak arises from the second term. In as much as the broader peak has a Gaussian shape, the height-height correlation function has a Gaussian distribution.
Figure 6-6: Laser Diffraction Profiles for Sample (a)
6.3 Out-of-Plane Profiles

Returning again to the time sequence data in figure 6-2, it is striking that the sharp specular peak disappears so rapidly. Often times, the disappearance of a sharp peak is an indication of a disordering process. However, in this case the sharp specular peak does not broaden at all as it disappears. Furthermore, after more time passes, the sharp specular peak reappears with low intensity. A more plausible hypothesis is that destructive interference causes the sharp specular peak to vanish as the depth of the fluctuations become comparable to the laser wavelength.

One way to test this hypothesis is to vary the momentum transfer out-of-plane which changes the effective out-of-plane wavelength. To perform this experiment, sample 9-93 was mounted on a 4-circle diffractometer. Figure 6-7 shows three scans at various $k_z$. These profiles confirm that the disappearance of sharp specular peak is due to destructive interference. This suggests that it may be possible to obtain the fluctuation depth by measuring the intensity of the sharp specular peak. More generally, information about the shape of the fluctuations can be obtained from scanning out-of-plane. Figure 6-8 shows the intensities, $I_n$ of the 0th through 3rd order peaks as a function of $k_z$. For these data, the polarization of the laser beam was in the scattering plane.

A sinusoidal surface profile, $H(x) = H_0 \sin(q_1 x)$ results in a scattering intensity

$$I(k) \sim \int \langle e^{ik_z H_0 \sin(q_1 x)} \rangle e^{ik_z x} dx$$

which reduces to

$$I_n \equiv I(k_n) \sim J_n(k_z H_0)^2 \quad k_1 = q_1. \quad (6.9)$$

where $J_n$ is an n'th order Bessel function. The profiles in figure 6-8 were fit to equation 6.9 after including polarization factors and factors which account for the decreasing intersection of the sample surface with the laser beam as $k_Z \to 0$. The fits are shown in figure 6-8 as solid lines. The high quality of the fits suggests that the surface modulation has an average amplitude of $\bar{H}_o = 0.4 \pm 0.05 \mu$ which is consistent

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Figure 6-7: In-Plane Diffraction Profiles as a Function of $k_z$
Figure 6-8: Out-of-Plane Laser Diffraction Profiles
with the AFM profiles of this sample in the previous chapter. The high quality fits also suggest that the modulation wavelength is narrowly distributed near $8\mu$. To the extent that equation 6.9 holds for $n = 2$, the modulation has no 2'nd order harmonics.

### 6.4 The Growth Rates of Fluctuations

As the previous sections suggest, the sharp specular intensity can be used to measure the fluctuation depth. *In situ* measurements can be used to determine the growth rate of the fluctuations. Here, the growth of the transverse fluctuations are studied between $1050^\circ\text{C}$ and $1200^\circ\text{C}$ with positive flowing in the step-down direction. Figure 6-9 shows the specular intensity as a function of normalized time where the normalizations, $t_n$, were chosen so that $t/t_n = 1$ at 40 percent of the initial intensities. The rates of growth as a function of temperature are proportional to $t_n^{-1}$. The $t_n^{-1}$ vs $1/T$ are plotted in figure 6-10. The straight solid line which is a fit to the data indicates that the energy associated with the growth is $E = 2.7 \pm 0.1 \text{ eV}$. Referring back to the energies of figure 4.4, it would seem that $E = E_n + E_a \simeq 3.0 \text{ eV}[11, 49]$. The discrepancy could easily be due to the uncertainties in $E_n$ and $E_a$. Once the theory of the transverse fluctuations is better developed, this laser measurement technique should provide persuasive measurements of the surface activation energies.
Figure 6-9: The specular intensity vs normalized time.
$E = 2.7 \pm 0.1 \text{ eV}$

Figure 6-10: The Fluctuation Growth Rate vs $1/T$. 
Chapter 7

Equilibrium Models

In this chapter, the theoretical and experimental progress in understanding the surface free energy is reviewed as it pertains to quasi-equilibrium growth and the equilibrium crystal shape. Here we define quasi-equilibrium growth to be growth where the rate limiting process is the transfer of material from the fluid phase to the solid phase. In this case, the surface is locally in equilibrium so that it has a well-defined free-energy. Quasi-equilibrium growth is an intermediate between the surface dynamics which was discussed in previous chapters and the equilibrium behavior discussed below. Jackson’s model of quasi-equilibrium growth introduces the phenomena of surface roughening which plays an important role in determining the equilibrium crystal shape.

7.1 Jackson’s Quasi-Equilibrium Crystal Growth

Experimentally, it is observed that some crystal growth occurs rapidly and isotropically while other crystal growth occurs relatively slowly and anisotropically. For example, the liquid-solid interfaces of metals often exhibit isotropic growth while non-metals and semiconductors often exhibit directional growth. In general, isotropic growth occurs on rough surfaces while directional growth occurs on smooth surfaces.

Following Jackson[29, 28], we review a macroscopic model of the growth process which provides a qualitative understanding of various growth phenomena. In this
model, the type of crystal growth depends on the parameter \( \alpha = \Delta S(x)T_m/\Delta E(x) \) where \( \Delta S(x) \) and \( \Delta E(x) \) are the entropy and energy of fusion for adding atoms from the fluid phase to the solid phase and \( T_m \) is the melting point. The fraction of surface sites occupied by adatoms, \( x \), provides a measure of the surface roughness. In general, the precise definition of "roughness" depends on the type of model used to describe the surface. Furthermore, the equilibrium and non-equilibrium mechanism for surface roughening can be different. However in each case, one expects that a "rough" surface is one for which long-wavelength fluctuations are governed by capillary forces. In Jackson’s model, roughening is defined at \( x = 1/2 \) which is realized in a sharp transition.

By assuming that the adatoms are independently distributed, simple approximations for the surface free energy, \( f = \Delta E(x) + T\Delta S(x) \), lead to the expression

\[
\frac{f}{k_B T_m} = \alpha x(1-x) + x\ln(x) + (1-x)\ln(1-x)
\] (7.1)

Figure 7-1(a) shows \( f(x) \) for several \( \alpha \). For large \( \alpha \), the surface free energy has minima at small \( x \) and \( 1-x \) corresponding to a smooth surface with a low density of adatoms and vacancies. On the other hand for small \( \alpha \), the surface free energy is minimized at \( x = 1/2 \) corresponding to a rough surface. The roughening transition occurs at \( \alpha = 2 \). The qualitative aspects of the surface for \( \alpha > 2 \) and \( \alpha < 2 \) are shown in figure 7-1(b). This simple theory predicts many of the empirical observations of fluid melt interfaces. For example, the liquid-solid interfaces of metals which have \( \alpha < 2 \) are rough whereas non-metals and semiconductor interfaces which have \( \alpha > 2 \) are more often smooth. Solids in contact with a vapor (metals included) typically have larger \( \alpha \) and are usually smooth. This concurs with the observation of directional growth of small metal crystals during heterogeneous deposition.

Since \( \alpha \) parametrizes some of the relevant properties of the surface, the growth dynamics are also correlated with \( \alpha \). The essential effect is the degree of undercooling, \( \Delta T \), necessary for a given growth rate. For a particular growth rate, large \( \alpha \) (or smooth surfaces) require large \( \Delta T \) whereas small \( \alpha \) (or rough surfaces) require only
Figure 7-1: Jackson’s Growth Model: The crystal surface free energy as function of the latent entropy of adding adatoms to the surface
small $\Delta T$. Jackson identified three general types of growth dynamics and reviewed theories which give the correct form of the growth rates, $R$, for each type of growth. On rough interfaces where there is a large density of energy barrier attachment sites for new adatoms, the growth is limited by diffusion or heat transfer: $R \sim \Delta T$. On smooth surfaces, where there is a low density of low energy barrier attachment sites, growth is limited by the rate of nucleation of two-dimensional islands: $R \sim \exp(T_0/\Delta T)$. Also on smooth surfaces, growth can occur primarily at defect structures in which case the growth is limited by the rate of diffusion to defect structures: $R \sim \Delta T^2$.

These theories are convenient in that they depend only on the macroscopic thermodynamic variables. However, despite the agreement in the functional forms of the growth rates, the absolute growth rates are not in agreement. In modeling growth, the position of the interface is often set by a temperature field. While this condition may be adequate for modeling macroscopic aspects of the growth on rough surfaces (small $\Delta T$), it may not be sufficient for modeling the growth of smooth surfaces (large $\Delta T$). In order to control the absolute growth rates in many situations, it is necessary to understand the role that atomic scale structure plays in the growth process.

### 7.2 Crystals at Equilibrium

The difficulty in obtaining quantitative confirmation of the BCF theory of crystal growth is due to the difficulty in measuring various equilibrium and kinetic parameters on the surface. For example, even though it is possible to measure many properties of the step configuration using diffraction and imaging techniques, it is not yet possible to observe the concentration of diffusing adatoms on the surface even if the step configuration is at equilibrium. However, many models of equilibrium have been developed in which the adatom concentrations are treated statistically.

Expressions for the surface free energy obtained from a particular model provide some direct comparisons with experiment. Wulff showed that the free energy of a crystal surface as a function of the surface orientation is related to the equilibrium crystal shape (ECS) such that cusps in the free energy at high symmetry orientations
create smooth facets on the ECS. Therefore, the disappearance of a cusp in the surface free energy is associated with a roughening transition at that orientation. This concept of roughening at equilibrium is analogous to concept the roughening during growth. Building on Wulff's work, Herring showed that the ECS can have curved regions connecting the facets and that the edges between the facets and curved regions can be either sharp or smooth. Calculations for a broad class of crystals has given the following progression: At \( T = 0 \), the equilibrium crystal shape consists entirely of smooth adjoining facets. For \( T > 0 \), the curved regions can form between the facets. As the temperature increases, the curved regions become larger and the facets become smaller. For each facet, there is a roughening temperature at which the facet disappears. If these roughening temperatures occur below the bulk melting temperature \( T_m \), then the roughening transition and the profile of the curved region provide a macroscopic tests of a particular model.

### 7.3 Equilibrium Profiles: Liquids and Crystals

In some cases, ECS's are governed by a surface tension similar to liquids. In these cases, the crystal surface is rough due to large wavelength fluctuations. In other cases, the ECS is governed by the lattice structure. Here a few expressions for the surface free energies and surface profiles for liquids and crystals are compared.

The equilibrium shape of a liquid droplet is obtained by minimizing the surface free energy

\[
F = \int \gamma dS
\]

(7.2)

where \( \gamma \) is the surface tension or free energy density. Since the surface tension of a liquid is isotropic, the equilibrium shape of a liquid drop is spherical. The surface profile is given by

\[
h \sim -x^2
\]

(7.3)

where \( x \) lies on a surface tangent and \( h \) is the distance of the surface from the tangent. Now consider an infinite liquid surface with orientation \( \hat{n} \). At \( T > 0 \), the surface will
exhibit large wavelength capillary waves so that the free energy is given by

$$F = \int f(x) \, dx$$  \hspace{1cm} (7.4)

where

$$f(x) = \gamma(1 + h_x^2)^{1/2}$$

$$\simeq f(0) + \beta h_x^2$$  \hspace{1cm} (7.5)

where the second term is associated with the surface fluctuations. Equations 7.3 and 7.5 are written in forms which emphasize the exponents in $x^\alpha$ and $h_x^\lambda$ respectively. These exponents can also be found for various models of crystal surfaces. Comparisons of experimentally measured exponents with theoretical predictions provide the simplest consistency test for a particular model. In the case of liquids, $\alpha = 2$ and $\lambda = 2$. These values are identical to the theoretical values obtained for rough crystal surfaces or for mean field step interactions as described below.

The equilibrium shape of a crystal is more complicated due to the effect of the lattice on the surface free energy density. The large wavelength analysis of fluids fails to take into account the atomic scale structure of a crystal surface. The TSK model is most easily investigated on vicinal surfaces with a finite step density $\rho$. For a vicinal surface, the surface free energy consists of the free energy of the terraces, $f(0)$, and the free energy associated with individual steps and the free energy associated with step interactions:

$$f(x) = f(0) + ag\rho(x) + H.O.T.$$  \hspace{1cm} (7.6)

where $g$ is the energy localized at a step of size $a$ and $\rho(x) = h_x/a$ is the density of steps. Herring showed that a cusp in the surface free energy produces a facet on the equilibrium crystal shape (ECS). Therefore in equation 7.6, the term linear in $\rho$ determines whether the ECS has the high symmetry facet. In fact, the size of the facet is proportional to the step energy, $g$. The H.O.T (higher order terms) contain terms higher order in $\rho$. The first non-zero H.O.T, $\beta(\rho)^\lambda$ is associated with the
exponent $\alpha$ of the profile of the curved region of the ECS near the facet edge,

$$h \sim -(x - x_0)^\alpha$$  \hspace{1cm} (7.7)

where $x_0$ is one-half the facet width. Therefore, both the step energy and the form the step interaction free energy is contained in the ECS profile.

### 7.4 Solid on Solid Models of Roughening

As BCF pointed out, the TSK model fails due to cooperative effects at high step and kink densities. This restriction is due to the assumption that the probabilities that a step or kink occur at a site are independent. At low temperatures where the density of steps and kinks are low, the TSK model is valid. However, at high temperatures where the density of steps and kinks is large, the correlations between surface fluctuations need to be considered. The solid on solid (SOS) model is designed to take cooperative effects into account. In the SOS model, the surface height can take only discrete values associated with the crystal lattice. In addition, fluctuations which create multi-valued surface heights are excluded. In general, the energy cost associated with nearest-neighbor height variations can be any increasing function of the height variation, $| h_j - h_{j+\delta} |$.

#### 7.4.1 The Two-Dimensional Ising Model

BCF made a first attempt to include these correlations by considering a surface confined to two surface planes. By assuming an energy cost for each nearest neighbor pair which occur at different planes, the surface Hamiltonian can be mapped to the 2-D Ising model of spin fluctuations. This is a special case of the SOS model. Onsager's exact solution to the 2-D ferromagnetic Ising model shows that the magnetization goes to zero above the Ising transition temperature due to large wavelength spin fluctuations. This result suggests that surfaces should exhibit large wavelength height fluctuations above a roughening temperature.
Figure 7-2: TSK and SOS Models
7.4.2 The Discrete Gaussian Model

The SOS model is a generalization of the 2-D Ising model which allows the surface height to take any of the discrete values associated with the crystal lattice. In SOS models, fluctuations which create multi-valued surface heights are excluded. In general, the energy cost associated with nearest-neighbor height variations can be any increasing function of the height variation, \( | h_j - h_{j+\delta} | \). Chui and Weeks\[9\] (CW) used a discrete Gaussian (DG) model to describe the roughening transition where the Hamiltonian of the surface fluctuations are quadratic

\[
H_{DG} = J/2 \sum_{j,\delta} (h_j - h_{j+\delta})^2
\]

(7.8)

Here the sum of \( \delta \) is over the nearest neighbors. For large wavelength fluctuations, Weeks\[54\] noted that

\[
H_{DG} \sim J/2 \sum_q q^2 h_q^2 \sim (J/2) h_x^2
\]

(7.9)

which is of the form of the free energy of a liquid, (see equation 7.5). On the other hand, since at low temperatures \( | h_j - h_{j+\delta} | \) is rarely greater than one interplanar spacing, equation 7.8 reduces to the form of the TSK model (see equation 7.6) at small length scales. Therefore, in the DG model, one expects that roughening of a high symmetry crystal surface occurs as the effects the large length-scale capillarity overtake the short length-scale rigidity of the lattice.

7.4.3 The Discrete Gaussian Model, the 2-D Lattice Gas and the XY Model

CW showed that the roughening transition of the DGM is related to the metal-insulator transition of the 2-D lattice coulomb gas. Using the renormalization technique Kosterlitz has shown that the 2-D lattice coulomb gas undergoes a metal to insulator transition at \( T_{MI} > 0 \) at which oppositely charged coulomb pairs are bound together below \( T_{MI} \) and but become unbound above \( T_{MI} \). On vicinal surfaces, this corresponds to a roughening transition at \( T_R > 0 \) where below \( T_R \). In the case of
the SOS, it is the vertical Fourier components of the lattice, $k_{j,n}$ which play the role of charges. The lateral interactions between the charges result from the lateral interactions represented in equation 7.9 and the distribution of the $h_j$. On a rough surface, the $k$ are localized whereas on a smooth surface the $k$ are de-localized. The DGM can also be mapped to the XY model which allows several results of the XY model to be carried over to the SOS model.[32, 33] As the temperature approaches $T_R$, the curvature, $\kappa$, of the surface approaches a positive constant value whereas below $T_R$, the curvature is zero which implies the formation of a facet on the ECS. The discontinuity in the surface curvature coincides with the surface stiffness, $\Gamma \sim 1/\kappa$, jumping to infinity.

The Ising and DG models both predict roughening transitions however, the nature of the singularities are different. Also, the DG model predicts a discrete jump in the surface curvature at $T_R$. Thus far no experiments have successfully measured the nature of the singularities. However, experiments on $^4He$ crystals have shown a jump in the surface curvature at $T_R$ which is consistent with the DG model. Both the Ising and DG models are designed to describe the roughening of a surface at high symmetry. For this reason, they do not provide predictions for the ECS profile which includes low symmetry orientations. This limitation is caused by the absence of corresponding representations of the H.O.T.'s in equation 7.6. Equation 7.9 may appear to be associated with a second order term in 7.6 however, as was already pointed out, equation 7.9 represents large wavelength capillary excitations whereas the H.O.T's of equation 7.6 represent the step interactions. Below $T_R$, these short range interactions determine the ECS in regions where capillarity is negligible.

### 7.5 Roughening of Vicinal Surfaces

The discontinuous jump in $\kappa$ at $T_R$ can also be stated in terms of the surface stiffness, $\Gamma \sim \kappa$, which is finite above $T_R$ and jumps to infinity at $T_R$. The infinite surface stiffness is associated with the appearance of the high symmetry facet. On the ECS one must also consider low symmetry orientations with a finite mean inclination from
the high symmetry axis. These surfaces are sometimes described as being "rough" below $T_R$ since the fluctuations of surface height due to step wandering have low energy. However when attempting to apply equation 7.6 to a low symmetry surface where $F(0)$ is the free energy of the flat low symmetry surface, one finds that the terrace-step description of the surface breaks down. Therefore, the SOS definition of roughness only applies to high symmetry surfaces. Furthermore, if only capillary forces were present, the ECS would be spherical, $\kappa = \text{constant}$, at all vicinal orientations except precisely at the facet orientation which is flat $\kappa = 0$. Since this is geometrically impossible, it follows that capillarity does not govern the fluctuations on a vicinal surface below $T_R$. Therefore, below $T_R$, vicinal surfaces are not precisely rough.

### 7.6 Critical Behavior from Step Interactions

The types of step interactions determine the critical exponents of the ECS. For a large class of simple, intuitive step interactions $\lambda = 3$ in contrast with the mean-field result which is $\lambda = 2$. Here, the theoretical models and predicted exponents are discussed for a variety of step interactions. Purely entropic interactions are discussed first, then modifications due to the presence of long-range forces are discussed.

In the absence of long-range forces, the interstep forces are entropic in nature. Entropic forces are short-range and arise from the constraint that the steps cannot cross each other. Entropic step interactions on vicinal surfaces can be mapped to the entropic interactions of domain walls which play a role in commensurate-incommensurate transitions. For this so called Pokrovsky-Talapov transition, $\lambda = 3$. This result is most easily obtained by mapping the entropic interactions of steps to the entropic interactions of one-dimensional fermions.[13] By filling the single-particle states up to the Fermi level $k_F = c$, the energy contained in all occupied states is

$$f_{\text{fermion}} \sim \int_0^{k_F} k^2 dk \sim k_F^3.$$  

(7.10)
Hence the result \( \lambda = 3 \). Any set of step interactions which do not introduce a second length scale in the step-step correlation function produces critical exponents identical to those of entropic interactions. On the other hand, the mean field behavior belongs to a different universality class.

Elastic and dipolar step interactions potentials have the form \( U(x) \sim g/x^2 \). An exact treatment shows that the contribution to the surface free energy due to these long-range forces is also of the form \( gc^3 \). Here a perturbation analysis shows that the interstep forces do not change the critical exponent. Using a Hartree-Fock approximation

\[
f_U \sim c \int_{0}^{\infty} dx U(x) G(x) \quad (7.11)
\]

where \( G(x) \) is the step-pair correlation function. Approximating \( G(x) \) by the fermion-pair correlation function

\[
G_{fermion}(x) = c[1 - \frac{\sin^2(\pi cx)}{(\pi cx)^2}] \quad (7.12)
\]

and substituting into equation 1 gives

\[
f_U \sim c^3 \int_{0}^{\infty} dy x^{-2}(1 - \sin^2 x/x^2). \quad (7.13)
\]

This implies that weak long-range interstep forces do not change the value of \( \lambda \).

This will hold as long as the long-range forces are not strong enough to significantly change the step correlations. If the step-pair correlation function is changed significantly, the result \( f_U \sim c^3 \) will still hold so long as \( G(x) \) has only one length scale – the step spacing – and the integrand in equation 7.13 does not diverge at small \( x \). If the correlations between the steps are influenced by other factors, critical exponents different from the Talapov exponents may be expected. The mean-field result, \( \lambda = 2 \), is obtained from equation 7.11 by setting \( G(x) = c \).
7.7 Lattice Calculations

The relative roughening temperatures of various facets depends on the energies of surface excitations for each facet. Models have been used to predict the behavior of the ECS for various facets of some simple lattices. Rottman et. al.[46] studied the three-dimensional Ising Model on a simple cubic lattice using mean-field calculations. Assuming attractive nearest neighbor interactions, $J_1$, they found that the thermo-evolution of the ECS depends on the strength of the second nearest neighbor interactions, $J_2 = R J_1$. For $R = 0$, only the (100) facet roughens at $T > 0$ — all other facets roughen at $T = 0$. For $R > 0$, which corresponds to attractive second nearest neighbor interactions, two additional facets — the (110) and the (111) exist at $T = 0$ and roughen at $T > 0$. For $R < 0$, which corresponds to repulsive second nearest neighbor interactions, only one additional facet — the (111) exists at $T = 0$ and roughens at $T_R > 0$. The facet edges are all smooth for $R >= 0$, but are sharp for $R < 0$. (Repulsive second nearest neighbor interactions may be expected in ionic salts such as NaCl.)

C. Jayaprakash et. al.[31] mapped the BCSOS model onto the six-vertex model of ferroelectrics. The (100) face of a BCC lattice is composed of atoms of two sublattices separated by $a/2$. Surface height fluctuations are due to truncation of the lattice at various (100) planes at different surface lattice coordinates. For a BBC lattice, this restriction limits the number of possible nearest neighbor configurations. By considering the sets of four surface atoms positioned on the vertices of a squares with diagonal $a$, there are only six unique elemental configurations. By assigning energies to each elemental configuration, the thermodynamic properties of the surface follow from evaluating the canonical partition function. This problem is identical to the six-vertex problem which is just one of many similar models used to model two-dimensional ferroelectrics. By using transfer matrix techniques, the six vertex model has been solved for the general case including external fields which create a net polarization. On the BCC (100) surface, the polarization corresponds to a mean inclination of the surface. In other words, the solution applies to surfaces vicinal to
the (100) surface as well. The exact result exhibits a roughening transition where above $T_R$, the ECS has the liquid-like profile whereas below $T_R$, the ECS has the step-fermion-like profile.

C. Jayaprakash and W. F. Saam[30] studied the (100), (110), and (111) surfaces of a face centered cubic lattice with attractive nearest neighbor interactions and attractive or repulsive second nearest neighbor interactions. Again the thermodynamic properties are derived from the results of the six vertex problem. However, here the energies of the elemental configurations are parametrized by the first and second nearest neighbor interaction energies. Below $T_R$, the surface profile has the form $z \sim x^{3/2}$ for all directions for the (100) and (110) faces. For repulsive second nearest neighbor interactions, some facet edges are sharp at certain temperatures. For attractive interactions, $\lambda = 3/2$. 
Chapter 8

Measurements of the ECS of Metals

8.1 Studies of Small Crystals

Experimental studies have confirmed many of the predictions of the SOS models. A common experimental technique is to grow small crystals and then to measure their equilibrium shape directly. This type of study has been performed for a large number of metals\cite{47, 37, 21, 22, 20, 52} and for $^4$He\cite{56, 8, 6, 3}. Roughening transitions have been reported for three facets of $^4$He; (0001), (10\overline{1}1), and (11\overline{2}2)\cite{3, 56}. These facets have smooth edges indicating second order orientational transitions. Furthermore, below the roughening transition, the ECS critical exponent near the (001) facet was measured to be $\lambda = 1.55 \pm 0.06$\cite{8} which is consistent with a Pokrovsky-Talapov transition. On the other hand, several facets on metals do not roughen below their melting points. These facets are for Pb: the (111) and (100) facets\cite{47, 22}; for In: (111) and (100) facets\cite{21, 37, 22}; for Au: (111) and (100) facets\cite{20}; and for Pt: (111) and (110) facets\cite{52}. Changes in growth rates have provided evidence of the roughening of the (110) and (11\overline{2}) facets of Pb and the (113), (131), and (011) facets of In\cite{22} For most metals, the facets have smooth edges indicating second order orientational transitions. Measurements of the ECS profiles indicate critical exponents of $\lambda = 1.6 \pm 0.15$ for Pb\cite{47} and $\lambda = 1.6 \pm 0.1$ for In\cite{37}. However, these
measurements are taken over a limited range of the profiles. Gold is an exception which shows sharp facet edges or first order transitions. For gold, the curved regions of ECS are spherical and the facet edges are circular in shape.

8.2 Studies of Vicinal Surfaces

Roughening can also be observed on surfaces which are constrained to a particular macroscopic orientation by their large size. Roughening of high-symmetry surfaces has been observed for several metals. X-ray studies of the (110) facets of Cu[39, 18] and Ag[17] indicate roughening transitions at 870 K and 725 K respectively. Similar studies of surfaces tilted slightly off the (110) axis have shown that the surfaces break up into a hill-and-valley structure below $T_R$ under certain conditions[16, 45, 43]. This can occur if the high symmetry orientation has a low enough free energy such that the total surface free energy is reduced by forming the high symmetry regions while increasing the total surface area. For repulsive step interactions, one does not expect faceting to occur. Step interactions can become attractive in the presence of surface reconstructions or adsorption. High step energies on the reconstructed surface can cause the steps to be squeezed together in unreconstructed regions. The same holds for facets which are stabilized by an adsorbate. Impurities are special cases of adsorption which can cause pinning of steps. This can also result in the formation of facets.

The Pt(001) surface undergoes a reconstruction transition above its roughening transition [58, 1]. Measurements of the unreconstructed ECS near Pt(001) using the reconstruction trick (see chapter 1) have indicated that $\lambda = 2.0 \pm .2$. This result can be compared with similar measurements of the unreconstructed ECS near Si(111) below the roughening transition. Experiments on vicinal Si(111) will be discussed in a later chapter.
8.3 Studies of Vicinal Ag(110)

A controversy has arisen concerning the faceting and roughening of vicinal Ag(110). In order for faceting to occur on a vicinal surface, the vicinal surface must be absent from the ECS. A number of studies have been performed using synchrotron x-rays.

Held et al[17] studied a vicinal Ag(110) surface with a miscut of 0.5°. They measured the scattering intensity near the (110) surface peak. At low temperatures, the scattering profile consisted of a central Gaussian peak and tails at large $\Delta q$. Near about 725 K, the central Gaussian peak disappears with increasing temperature. They interpreted their data as evidence of the roughening of the (110) facet. In a similar study, Robinson et al[45] studied a 0.2° miscut Ag(110) surface. Measurements were made at several locations along the $(1 + q_z, -1 + q_z, 0)$ truncation rod. Their data provide clear evidence of a faceting transition near 790 K with decreasing temperature. They interpreted the faceting below 790 K as indicating a sharp edge on the ECS at the border of the (110) facet.

In a second study, Held et al[17] studied a vicinal Ag(110) surface miscut by 1° toward the (110) direction. For a clean surface the single stepped phase was stable at all temperatures below 850 K. However, above about 800 K, sulfur impurities migrated to the surface from the bulk. These impurities cause the steps to be pinned. The pinned steps are accompanied by large (110) terraces or facets. The impurity ridden surface consisted of small (110) facets and stable uniform stepped regions. The existence of step bunches associated with the impurities was observed using STM for a 0.6 miscut.

8.3.1 Preparation of Vicinal Ag(110)

The Ag(110) surface is known for its instability during the preparation process. Successful preparation requires a careful balance of mechanical and chemical processing. In the studies by Held et al the preparation techniques were developed by Held and Mak following the recipe provided in the thesis of ???. The process involves repeated cycles of mechanical polishing with progressively finer Alumina polishing grit and chemical etching. In the final iteration a chemical polishing step is performed. X-
rays are often used to check the surface mosaic at various stages. The samples are typically cut about 2-3 mm thick from a boule about 1 cm in diameter. The sample is then mounted on a polishing jig with wax. Holding the jig by hand, the sample is polished on polishing paper mounted on a horizontal motorized wheel. The polishing paper is lubricated with polishing grit suspended in water. Polishing is a delicate procedure in which the weight applied to the Ag surface is controlled by hand. At the same time, maintaining the jig in a stable position on the wheel as it turns is made difficult by the small wheel size. Between grit sizes, care must be taken to clean all surfaces of all parts. This is accomplished by wiping with cotton swabs combined with ultra-sonic cleaning in detergent and rinse. Even a small amount of contamination by larger grits sizes will damage the surface. Using this procedure, producing a polished surface with a mosaic of 0.1° requires about 40 hours of labor assuming that the surface was not damaged at any stage.

The preparation of a miscut Ag(110) surface is identical to that of a Ag(110) surface except for a few points. First, the polishing jig must allow for the orientation of the sample to be adjusted to the correct miscut. Alignment of the sample was performed using x-rays by measuring the (110) Bragg peak for several crystal positions which are obtained by rotations along an axis near to the desired miscut. Compared with a standard polishing jig, this type of jig has many more parts which require repeated cleaning. It is also heavier which makes controlling the pressure applied to the Ag surface more difficult. It is also larger which makes the positioning on the polishing wheel less stable. These factors increase the risk of damaging the surface at some point during its preparation. It turns out that the orientation of the surface can not be set accurately until a high quality surface has been obtained. Furthermore, it is an empirical fact that only small corrections the the surface orientation can be made accurately. For these reasons, it is not uncommon to prepare four to eight high quality surfaces during the iterations of the surface orientation. The entire process of preparing a high quality surface with a specific miscut by this method requires about 300 to 500 hours of labor depending on luck and external factors.

After obtaining a polished surface, additional processing is required to reduce the
concentration of impurities in the sample. The original boule of Ag was specified as consisting of 99.9999% pure Ag by the manufacturer. However, the principle natural impurity in Ag is sulfur. Near the melting point of Ag, S is highly soluble in solid Ag, however the solubility decreases with decreasing temperature. It turns out that around 800 K, solubility is less than the impurity concentration and diffusion is rapid enough for S to diffuse over macroscopic distances to the surface on the time scale of our experiments. This results in the build up of S on the crystal surface. In order to purge S from the sample, the sample is treated with about 50 Ar ion sputtering and annealing cycles in ultra-high vacuum. Annealing periods ranged from 6 to 12 hours at about 800 K whereas sputtering to remove S from the surface required about 20 minutes and was performed at room temperature. Auger spectra were taken during each cycle to monitor the purging progress. Estimates of the amount of sulfur removed by this procedure indicate that the entire sample was being depleted of S. These one to two month purging procedures were performed in UHV chambers dedicated to sample preparation and testing. After purging the samples, they could be freely stored and transported in atmosphere.

8.3.2 The Experiment on Vicinal Ag(110)

Experiments were performed in the IBM "Wheel of Fortune" surface chamber using synchrotron x-rays at the MIT/IBM X20 Beamline at Brookhaven National Laboratory. Measurements were made through the \((1 + q_z, \bar{1} + q_z, 0)\) surface truncation rod near \(q_z = 0\) with a grazing incidence scattering geometry. Scans in the \((1\bar{1}0)\) direction (the direction of the miscut) provide information concerning the distribution of the surface normals. The intensity at a particular \(q_z\) consists of the sum of the truncation rods of the \((020)\) Bragg peak above the surface and the \((0\bar{2}0)\) Bragg peak below the surface. For a \((110)\) facet, these components coincide producing a single peak scanning in the \((1\bar{1}0)\) direction. For a stepped surface, the two components are split due to the tilted surface normal. The separation of the peaks provide means to measure the orientation of the stepped surface or equivalently the average step spacing. Faceted surfaces produce a central peak due to the facets and side peaks.
due to the stepped regions.

During the experiment, the surface was cleaned in situ by Ar ion sputtering followed by annealing at 800 K. Figure 8-1 shows the x-ray profiles at 373 K and 723 K from a set of data collected at a sequence of temperatures after annealing for 1/2 hour. Two peaks are present at all temperatures where the separation is independent of temperature. This indicates that a single uniform step phase is stable at all temperatures. On the other hand, figure 8-2 shows the longitudinal x-ray profiles at 473 K and 673 K from a set of data collected at a sequence of temperatures after annealing for 4 hours. In this case, a third central peak is present at low temperatures. The central peak is due to (110) facets on the surface while the two side peaks are due to the stepped regions. Since the separation between the step peaks is constant and consistent with the measured miscut of the surface, the facet regions are evidently accompanied by local step bunching due to impurities. This conjecture is supported by STM images. The increase of S impurities as a function of annealing time is consistent with the vast quantity of data obtained during the S purging procedure.

8.3.3 Discussion of Results

The disappearance of the central peak at 725 K coincides with the roughening temperature observed on Ag(110)[17]. Above the roughening temperature, there is no free energy cost for a step to move past an impurity leaving behind an island around the impurity, therefore the central peak should not be present above $T_R$. The fact that the decrease in the central peak occurs gradually can be explained by the gradual decrease in the free energy cost of bending around the impurities.

Although the studies of the 1° and 0.6° miscut surface do not exclude the possibility of a sharp edge on the ECS for which a range of orientations less than 0.6° are excluded from the ECS, it is consistent to re-interpret the faceting of the 0.2° miscut as the result of S impurities. The coincident disappearance of the (110) facets on impurity ridden 1° miscut surface and on smaller miscuts provides compelling evidence that the (110) facets roughen near 725 K.
Figure 8-1: X-ray Scans of a Clean Ag Surface
Figure 8-2: X-ray Scans of a Ag Surface with S Impurities
Chapter 9

The $7 \times 7$ Reconstruction Faceting

The most direct method of measuring the ECS is to measure the shape of small crystals at equilibrium. The method has been used to study the ECS of He and metal crystals. In these experiments, small crystal sizes are required in order for the crystal to attain its equilibrium shape in a practical length of time. On the other hand, if the crystal’s size is too small, the ECS may be modified by finite-size effects. Similarly on vicinal surfaces, the trade-off between equilibrium and finite-size effects occurs where the facet size and step band size determine the role of finite-size.

Measuring the ECS on a vicinal surface is further complicated by the difficulty in controlling the faceting length scales as the temperature is varied. It is evident that the facet size depends not only on temperature, but also on the heating rate and sample history. Therefore, a variety of cooling and heating treatments were used to study the process of phase separation.

9.1 Rapid Cooling and Slow Warming

The first treatment studied was the rapid cooling below $T_o$ followed by slow warming. After cooling the sample at a rate of about $10 - 20^\circ$ C per minute from the homogeneous phase to $796^\circ$ C, the sample was slowly warmed above $T_o$ over a period of many hours. This treatment was applied to a $3^\circ \rightarrow ^{<11\bar{2}>}$ Si(111) surface first with the electric current flowing in the step-up direction. Then after flashing the sample
for 1 minute at 1277° C, the same treatment was applied except with electric current flowing in the step-down direction.

### 9.1.1 Step-Up Current

X-ray scans along the $<11\bar{2}>$ direction were performed through the truncation rod of the $(11\bar{1})$ Bragg peak which lies above the surface with $H = 1$. A $(1,0)$ facet peak at $H = 1$ indicates that a component of the $(11\bar{1})$ truncation rod is parallel to the $<111>$ direction. This implies that a fraction of the surface is covered by $(111)$ facets. A $6/7$ th's peak at $H = 6/7 \approx 0.857$ arises from the $7 \times 7$ reconstruction on the $(111)$ facets. A step peak lying between the $6/7$ th's peak and the $(1,0)$ peak is due to step bands with orientations tilted by an angle, $\alpha$, from the $<111>$ direction producing a component of the $(11\bar{1})$ truncation rod lying at an angle, $\alpha$, from the $<111>$ direction.

Figure 9-1 shows the x-ray diffraction scans at several temperatures between 796° C and 873° C with the current flowing in the step-up direction. The initial cooling rate was about 10° C per minute. Immediately after cooling, the $(1,0)$ and $6/7$ th’s facet peaks appeared and were broadened due to the finite facet sizes. Several scans were taken at 796° C to establish the nature of time dependence. As a function of time, the $(1,0)$ and $6/7$ th’s peaks became sharper and more intense. Then as the temperature was raised, the combined effects of temperature and time dependence were observed. The average heating rate can be inferred from the time spent at each temperature point which was approximately one hour. Near $T_c$, the average heating rate was about 1° C per hour whereas at lower temperatures the average heating rate was as rapid as 20° C per hour.

The widths and shapes of the $(1,0)$ and $6/7$ th’s peak are always similar in our measurements which indicates that the $(111)$ facets are completely reconstructed and that the reconstruction is well ordered on the $(111)$ facets. The presence of the step-band peak below the $(1,0)$ facet peak indicates well defined step bands. Meanwhile the absence of a corresponding step peak near the $6/7$ th’s peak indicates that the step-bands and homogeneous phase are not reconstructed. The intensities of the facet
Figure 9-1: Warming Through $T_c$ for Step-Up Current
and step peaks between 796° and 873° C are shown in figure 9-2 while the widths of the facet peaks and the step peak are shown in figure 9-3. The behavior of these intensities and widths are useful in determining the transition temperatures and in identifying general trends.

At low temperature, a large intensity (1,0) peak and a smaller 6/7 th's peak from reconstructed (111) facets were measured along with a relatively small intensity step peak from step bands. Initially as the temperature was increased, the (1,0) peak intensity and width decreased suggesting that the fraction of the surface covered by (111) facets decreased. Near 860° C, the (1,0) peak intensity increased over a small range below 870° C before it decreased abruptly to near background levels between 870° C and 872° C. As the (1,0) peak disappears, its width decreases dramatically becoming resolution limited above 868° C. We will postpone discussing this temperature range until the discussion of the step density and surface profile.

The (1,0) and 6/7 th's peaks disappeared at about 870° C and 872° C which marks the nearly simultaneous un-reconstruction and un-faceting of the surface. Near the same temperature, the small intensity step-band peak is replaced by a relatively large intensity peak from a homogeneous step density phase. The step-band peak broadens dramatically before disappearing while the homogeneous phase step peak is sharp as it appears. This produces a sharp maximum in the measured step peak width at 870° C as shown in figure 9-3. The broadening of the step-band peak as the step bands disappear also creates a sharp minimum in the measured step peak intensity at 870° C as shown in figure 9-2(c).

Since the 6/7 th's peak disappears at 870° C and the step density above 870° C is equal to that of the homogeneous phase, $T_o$ is estimated to be 870 ± 0.5° C. The fact that the (1,0) peak disappears about 2° C higher at 872° C indicates a degree of step pinning as discussed in a later section. An alternative explanation is that a temperature gradient is present on the sample. However, the dip in the step peak intensity at 869° C shown in figure 9-2(c), which represents the breakup of step bands at $T_o$, would be broadened by a large temperature gradient, but would not be shifted significantly. Therefore, even with consideration of a temperature gradient, the best
Figure 9-2: X-Ray Peak Intensities Through $T_c$ for Step-Up Current
Figure 9-3: X-Ray Peak Widths Through $T_c$ for Step-Up Current
estimate of $T_o$ is about 870° C.

Figure 9-4(a) shows the step density, $c \sim 1 - H_{step}$, as a function of the sample temperature. The step density decreases between 800° C and 862° C then increases slightly between 862° C and about 869° C whereas above 870° C, the step density is equal to homogeneous phase density, $c_{macro}$. The increase in step density with temperature near $T_o$ is not consistent with the expected power-law dependence of the ECS.

To understand this result, it is useful to calculate the surface profile from the (111) facet size and the step density. The average (111) facet size, $L_{(111)}$, is equal to $\sqrt{2}\pi/\sigma_{(1,0)}$ where $\sigma_{(1,0)}$, is the finite-size (Gaussian) halfwidth of the (1,0) peak. The size of the step regions, $L_{step}$ is obtained from

$$L_{step} = \frac{c_{macro}}{c_{band} - c_{macro}}L_{(111)}. \quad (9.1)$$

Both $L_{(111)}$ and $L_{step}$ are shown in figure 5.1.4.

Near $T_o$, the average facet size increases by more than a factor of two. Apparently, the rapid cooling produces relatively small facets which then grow during slow heating due to coarsening. This coarsening of the facets is concurrent with the increase in step density and the decreasing step correlations near $T_o$. The increase in the step density suggests that the ECS and surface free energies depend on the faceting wavelength as shown in figure 4.2(b). Since the step-band size is much greater than the step correlation length, the decreasing step correlations indicate increasing step disorder. This disorder is probably introduced as the step-bands are reshaped during coarsening.

### 9.1.2 Step-Down Current

The case of rapid cooling and slow warming with electric current flowing in the step-down direction is presented in figure 9-5. Figure 9-5 shows the x-ray diffraction scans along the $<11\bar{2}>$ direction at several temperatures between 796° C and 872° C. Here the cooling rate was about 20° C per minute while the warming rate was about
Figure 9-4: Surface Profile Through $T_c$ for Step-Up Current

- (a) Step Density, $c$ [R.L.U.]
- (b) (111) Facet
- (c) Step Band
0.5° C per hour near $T_o$ and about 20° C per hour below about 850° C.

The nature of the reconstruction transition for the step-down current direction is fundamentally different from that of the opposite current direction in that a step bunching instability occurs both above and below $T_o$. Initially, the surface was prepared with a homogeneous step density by flashing with the current flowing in the step-up direction. After reversing the current to the step-down direction and cooling rapidly to 796° C, the facet peak appeared and was broadened by finite-size effects similar to the case of current flowing in the step-up direction. However, the time dependencies of the facet peak widths and intensities are opposite to those for the step-up current direction. Instead of sharpening and intensifying with time, the facet peak broadened and became less intense with time. Furthermore, the shape of the x-ray scattering profile from the step bands developed a complicated structure as the temperature increased. As the step density of the step-bands decreased, many small, sharp features appeared between the step peak and the (1,0) peak. In the presence of the reconstruction, the (1,0) peak was broad. As the (6/7) th’s peak disappeared, the broad (1,0) peak also disappeared. However, soon a sharp (1,0) peak appeared and grew in intensity. Meanwhile, after the step peak became centered around the homogeneous phase position, it broadened dramatically as large shoulders appeared on each side of the central feature.

This complicated behavior is probably due to two faceting mechanisms competing at different length scales. Initially, small facets are locked in by the reconstruction. As the reconstructed regions decrease in size, the current driven faceting instability at a large length scale reorders some of the step-bands perhaps forming a large wavelength modulation of the surface. When the reconstruction disappears, the steps are no longer locked into small step bands and are distributed around the homogeneous density. However the current driven faceting proceeds by producing a modulation in the step density on a large length scale. This results in a broadening distribution of step densities. Eventually, large (111) facets are formed together with highly disordered stepped regions.

Figures 9-6 and 9-7 show the facet and step peak intensities and widths obtained
Figure 9-5: Warming Through $T_c$ for Step-Down Current
from fits of the x-ray scans to Gaussian peak shapes between 796° C and 872° C. Below 850° C, the step peak sharpens and increases in intensity with temperature which is qualitatively similar to its behavior for a step-up current direction. However, above 850° C, the behavior is different. Instead of broadening below \( T_o \), step peak broadens and increases in intensity above \( T_o \). This causes a maximum in the step peak intensity to occur at 867° C. Below 867° C, the (1,0) peak decreases in intensity and broadens with increasing temperature whereas above 867° C, the (1,0) peak increases abruptly in intensity and sharpens abruptly to the resolution limit. The behavior of the 6/7 th's peak is similar to that of the (1,0) peak below 867° C. However the 6/7 th’s peak disappears between 867° and 868° the point where the (1,0) peak undergoes abrupt changes. This indicates that \( T_o \) is 3° C lower for current flowing in the step-down direction that for current flowing in the step-up direction.

Figure 9-8 shows the step density and the calculated facet and step-band sizes. Below 867° C, the step band density decreases monotonically which could possibly be a power law dependence over some range. Furthermore, the (111) facet size decreases instead of increasing as in the case of the opposite current direction. Meanwhile, the step-band size increases which results in the faceting wavelength remaining approximately constant. Therefore, it may be appropriate to conclude that below 867° C, quasi-equilibrium behavior is being displayed. However, instead of proceeding by attempting to measure the critical exponents, this will be postponed until the next chapter where a more systematic data set is discussed.

### 9.2 Slow Warming, Slow Cooling

In the previous sections, \( T_o \) associated with the phase separation was identified. However \( T_c \) has yet to be determined. For this purpose, additional data are presented here that were collected during a second very slow warming and slow cooling with current flowing in the step-up direction.

After the slow warming to 871° C with current flowing in the step-down direction, the current was reversed to the step-up direction and the sample was allowed to
Figure 9-6: X-ray Intensities Through $T_c$ for Step-Down Current
Figure 9-7: X-ray Widths Through $T_c$ for Step-Down Current
Figure 9-8: Surface Profile Through $T_c$ for Step-Down Current
anneal for three days. After about six hours of annealing, a sharp step peak from a homogeneous phase and sharp (1,0) and 6/7 th's peaks were present and remained visibly unchanged for the remainder of the anneal. After three days, the sample temperature was raised in approximately 1/4° C steps to above 874° C. The measured (1,0) and 6/7 th's peak intensities are shown in figure 9-9 as open circles. Both peaks approach background levels at 873.25 ± 0.25° C. This is about one or two degrees higher than for the (1,0) peak during the first slow warming which is also shown in figure 9-9 as open squares.

After the second slow warming, the sample was flashed for 1 minute at 1277° C then cooled slowly through the phase separation at a rate comparable to the first slow warming (about 1° C per hour). The measured (1,0) and 6/7 th's peak intensities are shown in figure 9-9 as solid circles. Here the (1,0) peak appears at about 3° C below the point at which it disappeared during the second warming and about 1° C below that of the first warming.

Differences in the measured phase separation temperatures can be caused by several effects. The absolute temperature measurements can vary several degrees from one sample to another due to many factors which affect the error of measurement. However, on a single sample which has not undergone extreme treatment, the temperature measurements are reproducible within 1° C. Therefore measurement errors do not account for the full range of measured temperature variations. Metastability can cause a difference between cooling and warming phase separation temperatures. However since metastability is not relevant during warming, it cannot account for the temperature variations during warming even if the heating rates are different. On the other hand, hysteresis can cause temperature variations to be observed during warming or cooling the surface.

Hysteresis is a common phenomenon of first order phase transitions which, in the case of a vicinal surface, can be caused by step pinning. Steps may become pinned or trapped by the presence of impurities or defects on the surface. Pinned steps may prevent small regions near the pinned steps from obtaining their equilibrium density of steps. The region on one side of a pinned step may have an excess of steps whereas
Figure 9-9: Hysteresis in X-Ray Peak Intensities for Step-Up Current
the region on the opposite side may have a deficiency of steps. During warming, the regions with a deficiency of steps will remain reconstructed up to higher temperatures than will regions far from any pinned steps. In the limit of zero step density regions, the reconstruction will disappear at $T_c$. If the steps remained pinned above $T_c$, these regions provide nucleation sites for faceting during cooling. Therefore pinned steps may cause the phase separation temperatures observed during warming and cooling to approach $T_c$.

The lineshapes of the step peak above $T_c$ provide evidence of step pinning. In figure 9-10, several differences are evident in the x-ray profiles at 881° C after the first and second slow warmings. The step peak is much sharper and the tails of the step peak lineshape are more prominent after the second warming than after the first warming. In addition, a second order step peak due to the truncation rod of the (002) Bragg peak below the surface is present after the second warming. The sharpness of the first order step peak is the combined result of the flashing which was performed between the two warming runs and the three day anneal at 871° C with current flowing in the step-up current direction. Previously, we determined that repeated flashing can cause the appearance and growth of the second order step peak. In this case however, the first appearance of the second order step peak is undocumented. Therefore, it is unclear whether the three-day anneal played a role in generating the second step peak.

On a time scale of hours, the intensities and widths of the first and second order step peaks above $T_c$ and with current flowing in the step-up direction depend on the sample preparation (warming above about 1100° C). On the other hand, the intensities and widths are largely unaffected by cooling and warming through $T_o$. In contrast to this independence, the tails of the step peaks depend on the history of cooling and warming through $T_o$. For rapid cooling and warming through the transition, the step peak lineshapes are unchanged whereas for very slow warming or very slow cooling through the transition, the tails become more prominent. Once prominent tails have formed, the only way that they can be reduced is to flash the sample.

The changes in the lineshape of the first order step peak are correlated with
Figure 9-10: X-Ray Scans After Two Warmings for Step-Up Current
the occurrence of a streak in the laser diffraction pattern from the sample surface. The pattern observed from the surface of figure 9-10(a) consists of a sharp, circular, specular spot which is consistent with its mirror-like appearance. On the other hand, the pattern observed from the surface of figure 9-10(b) consists of a sharp specular spot with a transversely sharp streak running along the $<11\bar{2}>$ longitudinal direction. The streak first appears during facet coarsening as the facet wavelength approaches about one micron which only occurs by warming or cooling the sample sufficiently slowly. Once the streak appears, it remains after heating above $T_c$. Like the tails in the lineshape of the step peak, the only way that the streak can be reduced is to flash the sample.

The prominent tails in the step peak lineshape indicate that there is significant amounts of small wavelength fluctuations in the step density. On the other hand, the streak in the laser pattern indicates that there are significant amounts of large amplitude, large wavelength fluctuations in the surface profile. Together these two types of fluctuations suggest a step configuration similar to the result expected from step pinning at localized pinning sites. The absence of the (1,0) peak above $T_c$ but with significant amounts of step pinning can be explained by assuming that in the absence of the $7 \times 7$ reconstruction, the steps (or step bands) lose their rigidity. Since the pinning sites are localized, the steps can bend around the pinning sites reducing the correlation lengths of the (111) facet regions and thereby reducing the (1,0) peak.

Given the evidence of step pinning provided by the x-ray lineshape and the laser diffraction pattern, the intensity measurements in figure 9-9 provide an estimate of $T_c$. The effects of pinned steps whether due to impurities or intrinsic defects should be most prevalent on surfaces which have been below impurity sublimation temperatures for long periods of time or which have undergone extensive coarsening. Both the first warming and the second cooling of figure 9-9 occurred shortly after flashing the sample. On the other hand, the second warming occurred after being annealed at facet coarsening temperatures for three days. Therefore, it is not surprising that the phase transition for the second warming occurred at the highest temperature. This temperature will be used to estimate $T_c$ (i.e. $T_{c}^{est} = 873^\circ$ C).
It is interesting that the phase separation temperature for the first warming is within one or two degrees of $T_{cst}$ even though it occurred only a short time after flashing. This suggests that coarsening alone can cause step pinning or more generally hysteresis. Intuitively, this is consistent with the increased stability of step bands due to coarsening as shown in figure 1-4(b).

Between each of the warming and cooling treatments, in figure 9-9, the surface was flashed once for one minute at 1277°C. For the purpose of measuring hysteresis, these flashings were unfortunate. Nevertheless, the data in figure 9-9 provide valuable information concerning hysteresis. The effect of the flashing between the first and second warmings was only partially documented. However, the treatment at opposite current direction and the long annealing and coarsening periods further diminish the topological "memory" between the two warmings. The flashing between the second warming and the first cooling was not sufficient to reduce effectively the tails in the lineshape and the streak in the laser pattern. Therefore, the 3°C shift in the phase transition temperature is attributed to hysteretic behavior. The alternative explanation is that the shift is due to metastability and the temperature difference in $T_{sp}$ and $T_o$. However evidence provided by rapid cooling and rapid heating indicate about a 7°C difference in $T_{sp}$ and $T_o$ on a 3° miscut. This treatment is discussed in the next chapter.

From one sample to another, the measured values of $T_o$ and $T_c$ may be offset by various systematic errors in the temperature measurement. However, the result that $T_c - T_o = 3°C$ should hold for each set of measurements on a 3° miscut sample. This result will be useful in measurements of the critical behavior of the ECS on a sample for which $T_c$ is unknown.
Chapter 10

The ECS for Two Current Directions

In order to study the metastability of the homogeneous phase and to measure the spinodal temperature, it is necessary to reduce the amount of coarsening and hysteresis. This can be achieved by cooling and warming rapidly through the phase transition. However, collecting data during rapid temperature change is difficult if scans of \( H \) must be performed at various temperatures. This is because each \( H \) scan takes at least several minutes to perform. Therefore, a better technique is to select values of \( H \) and perform temperature scans with a high density of temperature points and equal counting times. The fixed cooling and heating rate provides better control of the average faceting wavelength.

10.1 Step-Up Current Direction

By selecting \( H \) at a peak position, the peak intensity can be measured as a function of temperature. Figures 10-1(a) and (b) show the peak intensities of the (1,0) and 6/7 th’s facet peaks and the homogeneous phase step peak for cooling and warming rates of 5° C per minute. Since the position of the step peak is a weak function of temperature above \( T_c \), a small linear adjustment of \( H \) was made at each point while scanning temperature. As a function of temperature, the (1,0) and 6/7 th’s
facet peaks disappear at about the same temperature that the homogeneous phase step peak appears during both cooling and warming. These points mark the phase separation temperatures.

During cooling, the phase separation occurs at $T_{sp}$ due to the metastability of the homogeneous phase while during warming, the phase separation (or convergence) occurs at $T_o$. From figure 10-1, the values of $T_{sp}$ and $T_o$ are about 857°C and 864°C respectively. These values of $T_{sp}$ and $T_o$ do not depend on the cooling or warming rates in the range of 40°C per minute to 1°C per minute. The temperature difference $T_o - T_{sp} = 7 \pm 1°C$ for a 3° miscut is consistent with LEED[25] measurements on a wide range of miscuts and is reproducible on our various samples.

In addition to peak intensities, the peak widths and positions can be measured by scanning the temperature at numerous $H_i$. As the step peak moves through $H_i$, a maximum occurs at a particular temperature, $T_i$. The total data set consists of a two-dimensional mesh of intensity values for cooling and warming. The pairs of values $(T_i, H_i)$ determine a curve which is closely related to the free energy curves of the type shown in figure 1-4(b). By fitting the peak position of the $T$ scans, the $T_i$ can be found to great precision while the $H_i$ are accurate to the limit of the spectrometer alignment. In theory by selecting a large number of $H_i$, $c_{band}(T)$ can be found with great precision.

Temperature scans were performed for a ramp rate of 1°C per minute for both cooling and warming. Examples of warming temperature scans at various $H_i$ are shown in figure 10-2. At the homogeneous step peak position, $H_{homo} = 0.9814$ R.L.U., the intensity increases between 868°C and 878°C due to the appearance of the homogeneous step peak just as in figure 10-1. As $H_i$ is moved away from $H_{homo}$, the component of the intensity due to the homogeneous phase decreases while a component due to the step bands becomes better resolved.

In order to determine the $T_i$, the scans were fit to the sum of an error function and a Gaussian lineshape. The error function is used to represent the intensity from the homogeneous phase while the Gaussian peak is used to represent the intensity from the step bands. Since the peak due to the step bands is an asymmetric function of
Figure 10-1: Peak Intensity vs Temperature for Step-Up Current
Figure 10-2: Temperature Scans for Step-Up Current
temperature, it was convenient to use a drifting Gaussian halfwidth, \( \sigma = \sigma_0 + \Delta T \sigma_1 \). By fixing the location of the error function at the \( T_i \) determined for \( H_i = H_{\text{homo}} \), the step band intensity can be measured as it appears or disappears. Some of the fit lineshapes are shown in figure 10-2.

The fit parameters of the temperature scan lineshapes indicate the behavior of the step bands. The Gaussian and error function amplitudes are shown in figure 10-3. At low temperatures, the Gaussian amplitude increases with \( T_i \) while the error function amplitude remains small. As \( T_i \) crosses the phase transition, the Gaussian amplitude first decreases slightly as the error function amplitude increases, then the Gaussian amplitude increases sharply before disappearing. The sharp increase in the Gaussian component is due to the difficulty in resolving the step band intensity as the step peak approaches \( H_{\text{homo}} \). Therefore, the dip in the Gaussian amplitude indicates the region of phase separation. Above this region, the Gaussian component does not well represent the behavior of the step band intensity.

Figure 10-3 indicates that the phase separation occurs near 858\(^\circ\) C during cooling and near 865\(^\circ\) C during warming. This is consistent with the previous finding that \( T_o - T_{sp} = 7 \pm 1\(^\circ\) C \) however, the present measurements are less precise. More precise determinations can be made from the measurements of the step density. The measurements, \((T_i, H_i)\), are shown for both cooling and warming as solid circles in figure 10-4. Also shown are contours of the total data set for both cooling and warming.

In contrast with the case of rapid cooling and slow warming, the step density is a monotonic function of temperature for both cooling and warming. During cooling, the step density begins to deviate from the homogeneous phase density near 860\(^\circ\) C whereas during warming the step density approaches the homogeneous phase density near 870\(^\circ\) C. However on warming, there is a region of upward curvature in the \((T_i, H_i)\) which is not apparent in the contours. In light of the previously mentioned difficulty in resolving the step band intensity near the phase separation, the upward curvature in \((T_i, H_i)\) is attributed to an artifact of the fitting procedure while the true step density always curves downward as indicated by the contours. The range of upward
Figure 10-3: Temperature Scan Intensities for Step-Up Current
Figure 10-4: T-H Mesh for Step-Up Current
curvature will be excluded when determining the critical behavior of the ECS in the next section. The contours suggest that the step density approaches the homogeneous phase density near 867° C. Here again, \( T_o - T_{sp} = 7 \pm 1° C \).

It has been postulated that the critical behavior of the ECS may be determined by fitting the critical exponent of the step density

\[
c = c^\ast(T_c - T)^\lambda.
\]  

(10.1)

In order to confirm a power law relation, the fit values of \( \lambda \) and \( T_c \) should be independent of the range of data fitted. Furthermore, recalling that the true critical exponent is expected to hold only in a limited range near \( T_o \), it is desirable to determine \( \lambda \) from a small range of temperature.

Previous determinations of \( \lambda \) have suffered from the difficulty of obtaining a high density of data points near \( T_c \). Therefore fitting over a large temperature range was required. On the other hand using the method of scanning temperature, \( \lambda \) can be evaluated very close to \( T_o \) on surfaces with small miscuts.

The step density was measured over the range \([680°, 900°] \) C for constant cooling and warming rates. Over most of the temperature range, the step density changes approximately linearly with temperature except for a small range near \( T_o \) where the step density changes more rapidly and below 750° C where the step density begins to saturate. The linear behavior does not follow a power law form because the temperature intercept does not occur at \( T_c \). Therefore \( \lambda \) must be determined from the curved region near \( T_c \). Since during cooling the available range is limited to below \( T_{sp} \), it is advantageous to determine \( \lambda \) from warming data.

Due to the uncertainty in the evaluation of \( T_c - T_o = 3° C \) for a 3° miscut, fits of the warming measurements of \( c(T) \) to equation 10.1 over various ranges were performed first by letting \( T_c \) vary and then by holding \( T_c \) fixed. The upper boundary of the range was fixed at 865° C in order to exclude the region of upward curvature described above. The lower boundary was varied from 815° C to 860° C. The fit values of both \( \lambda \) and \( T_c \) depend on the range selected. The fit values of \( \lambda \) as a function of
the lower boundary are shown in figure 10-5(a) as open circles while for each fit value of \(\lambda\), the fit value of \(T_c\) is shown by open triangles. As the fit range becomes small, \(T_c\) approaches about \(870^\circ\) C and \(\lambda\) approaches about 3. On the other hand as the range becomes large, the fit values of \(T_c\) increase above \(877^\circ\) C and the fit values of \(\lambda\) decrease below 2. Two representative fit curves with \(\lambda \approx 2\) and 3 are shown in figure 10-5(b).

As expected, the fit curve for \(\lambda \approx 2\) follows the data over a wider temperature range than for \(\lambda \approx 3\). However, for \(\lambda \approx 3\) the fit curve more closely follows the curvature of the data near \(T_\phi\). Ideally, an independent measurement of \(T_c\) on a (111) surface would be useful in determining the best value of \(\lambda\). \(T_c\) is often reported to be \(870^\circ\) C. However, our temperature measurements often vary by several degrees from one sample to another. Therefore, literature values of \(T_c\) are difficult to use. The best independent measure of \(T_c\) may be provided by the study of hysteresis during slow cooling and warming described earlier. There we concluded that \(T_c - T_\phi = 3 \pm 0.5^\circ\) C. The fact that on this sample \(T_\phi = 867 \pm 0.5^\circ\) C, implies that \(T_c = 870 \pm 1^\circ\) C.

By fixing the value of \(T_c\), the fit values of \(\lambda\) can be obtained more precisely. The fixed value of \(T_c\) was selected by first fixing \(\lambda = 3\) and fitting \(T_c\) over several ranges. The fit value of \(T_c\) was found to be independent of the fit range for a lower boundary greater than \(8450^\circ\) C. For the range \([8450^\circ, 8650^\circ]\) C, the fit value of \(T_c\) was \(870.04^\circ \pm 0.2^\circ\) C whereas for the range \([8600^\circ, 8650^\circ]\) C, the fit value of \(T_c\) was \(870.07^\circ \pm 0.5^\circ\) C. Therefore, the fixed value of \(T_c\) was chosen to be \(870^\circ\) C. With \(T_c\) fixed, the fit values of \(\lambda\) as a function of the lower boundary are shown in figure 10-5(a) as solid circles. As one expects, the value of \(\lambda\) is close to 3 for a lower boundary greater than \(8450^\circ\) C. By this method, the fit values of \(\lambda\) and \(T_c\) were found to be independent of the fitting range above \(8450^\circ\) C. This fact increases the confidence in the determination of a power law behavior. The best estimate of the critical exponent based on our measurements is \(\lambda = 3.0 \pm 0.1\).

The premise for the success of this measurement is that the faceting wavelength is constant during the warming temperature scans. This can be confirmed by determining the width of the step peak as a function of temperature. For this data set,
Figure 10-5: Critical ECS for Step-Up Current
the density of temperature points is about one point per degree. Therefore by taking slices of 1° C width, the $H$ profiles can be constructed with a resolution of 1° C. This represents a great improvement in resolution over the method of scanning $H$ as a function of $T$ which is frustrated by time dependent effects. In figure 10-6, $H$ profiles are shown for two temperatures above $T_o$ and one temperature below $T_c$.

The profiles were first fit with a single peak plus background terms. The resulting peak halfwidths are shown in figure 10-7 as solid circles for both cooling and warming scans. The quality of the fits near and above $T_c$ are limited by having collected data on only the lower half of the peak profile. Nevertheless, figure 10-7 shows that the step correlations are nearly constant below $T_o$. This suggests that coarsening is not occurring to a significant degree.

Next, the warming profiles were fit to two peaks plus background terms. The position and width of one peak was fixed at the homogeneous peak position and width while allowing only the amplitude to vary. For the second peak, the position, width, and amplitude were allowed to vary. Some of the fit profiles are shown in figure 10-6. At 875° C, the second peak amplitude is zero while at 868° C and 860° C, components of both peaks are present. It is interesting the that second peak is present above $T_o = 867° C$ where a single homogeneous phase is expected. The behavior of the position and width of the second peak suggests that above $T_o$ the second step peak is due to a small amount of step pinning.

The width of the second peak as a function of temperature is shown in figure 10-7(b). The width of the second peak approximately doubles above 867° C. This behavior can be explained by a some amount of step pinning which creates small step bunches with step densities close to the homogeneous density. Figure 10-6(b) shows the width of the second step peak decreases sharply at 870° C. Above 870° C, the second peak position and width are similar to the first peak so that the two peaks cannot be resolved. This indicates that the broad peak disappears at 870° C and suggests that the amount of step pinning is reduced dramatically at 870° C. The fact that this occurs at $T_c = 870° C$ suggests that the disappearance of the reconstruction near the pinned steps plays a role in the unpinning of the steps. If this is indeed
Figure 10-6: Peak Profiles for Step-Up Current
Figure 10-7: Peak Widths for Step-Up Current
the case then the unpinning of steps can provide a measure of $T_c$ even during rapid warming and cooling.

### 10.2 Step-Down Current Direction

The treatment of rapid warming was used to study the ECS for current flowing in the step-down direction as well. Measuring the ECS for the current direction is more difficult for the step-down current direction because the homogeneous phase is unstable above $T_c$. However since the reconstruction faceting occurs almost instantaneously whereas the current driven faceting occurs slowly, it is possible to measure the ECS by rapid cooling and warming if the data are collected over a short period of time.

The ECS can be studied by performing temperature scans at various $H_i$. Temperature scans for three $H_i$ are shown in figure 10-8. In order to determine the $T_i$, the profiles were fit to the sum of a Gaussian and an error function. Again the homogeneous step peak intensity is represented by the error function while the step band intensity is represented by a Gaussian with a drifting halfwidth. Some of the fit profiles are shown in figure 10-8.

The amplitudes of the Gaussian component and the error function component as a function of temperature are shown in figure 10-9. In the case of cooling, the Gaussian component is maximum near $858^\circ$ C and decreases to zero at $862^\circ$ C. For the case of warming, the Gaussian component is maximum near $858^\circ$ C and decreases to zero at about $863^\circ$ C. In contrast to the case of current flowing in the step-up direction, a sharp increase in the Gaussian component before disappearing is not observed. This indicates that here the fitting procedure is better able to resolve the step-band intensity near $T_c$.

The points where the Gaussian components decrease to zero are associated with the phase separation temperatures. However, these temperatures can be determined more accurately from the step band density.

The step band density as a function of temperature represented by the points $(T_i, H_i)$ are shown in figure 10-10 for both cooling and warming. Also shown are
Figure 10-8: Temperature Scans for Step-Down Current
Figure 10-9: Peak Intensity for Step-Down Current
contours obtained from the two-dimensional mesh of intensity measurements. During cooling the step density approaches the homogeneous step density at $860 \pm 0.5^\circ C$ whereas during warming the step density approaches the homogeneous step density at $862\pm0.5^\circ C$. If metastability is responsible for the lower phase separation temperature during cooling then $T_0 - T_{sp} = 2^\circ \pm 1^\circ C$ which is less than for the step-up current direction.

The critical exponent of the ECS can be determined by fitting the step density to a power law of the form of equation 10.1. The fitting procedure followed here is similar to that for the step-up current direction. First both $\lambda$ and $T_c$ were allowed to vary then $T_c$ was fixed and $\lambda$ was allowed to vary. The fits were performed over various ranges $[T_{lower}, 864^\circ]$ C where $830^\circ C < T_{lower} < 860^\circ C$. Figure 10-11 shows the fit values of $\lambda$ as a function of $T_{lower}$. For variable $T_c$, the fit values of $\lambda$ are shown as open circles. For each fit value of $\lambda$, the corresponding fit value $T_c$ is shown as open triangles. As the fitting range becomes smaller, the fit value of $\lambda$ approaches 3 and the fit value of $T_c$ approaches 866$^\circ$ C. The fit power laws determined for a fitting range $[850^\circ, 864^\circ]$ and $[830^\circ, 864^\circ]$ ($\lambda = 2$) are shown in figure 10-11(b). As expected, the curve for $\lambda = 2$ follows the step density over a wider range however, the curve for $\lambda \approx 3$ more closely follows the curvature of the step density near $T_c$.

In order to select a fixed value of $T_c$, $T_c$ was fit over various ranges with $\lambda$ fixed at 3.00. For a fitting range above $845^\circ$ C, the fit value of $T_c$ was $865.8 \pm 0.2^\circ C$. Therefore, the fixed value of $T_c$ was chosen to be $866^\circ$ C. Recalling that $T_c$ was determined to be $870^\circ$ C for the step-up current direction, this implies that $T_c$ is $4 \pm 1^\circ$ C lower for the step-down current direction. This is consistent with the difference of $3 \pm 1^\circ$ C determined by the treatment of rapid cooling and slow warming. With fixed $T_c$, the fit values of $\lambda$ are shown in figure 10-11(a) as solid circles. Again as one expects, $\lambda \approx 3$ for $T_{lower}$ greater than $845^\circ$ C.
Figure 10-10: T-H Mesh for Step-Down Current
Figure 10-11: Critical ECS for Step-Down Current
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