DOMAIN BOUNDARIES OF THE 5×5 DAS RECONSTRUCTION

by

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For Alison
Abstract

Steps on surfaces have long been explored for their own sake, and exploited as growth mediators. However, another type of linear surface defect - the domain boundary - has been largely neglected. Here we introduce domain boundaries of the $5\times5$ dimer-adatom-stacking fault reconstruction, explore their properties and demonstrate that they too can be used to mediate growth in a useful manner.

When a thin layer of Ge is grown on Si(111) lattice strain induces the overlayer to reconstruct as Ge$5\times5$. Using solid phase epitaxy, many domains of $5\times5$ can be grown. The domain interiors have excellent order, and with careful annealing, the boundaries that separate them are straight and uniform. Well-ordered boundaries propagate along the two high symmetry directions $\langle1\bar{1}\rangle$ or $\langle11\rangle$ and are called A-type or B-type respectively. Boundaries of the second type are unique to Ge$5\times5$. Registration with the substrate restricts the misfit between domains to discrete possibilities which are labeled according to a modified version of the system used for domain boundaries of Si(111)$7\times7$. The distribution of observed boundary types is strongly peaked and reflects the relative energies of boundaries of different character. The expanded labeling scheme can be used to sketch the kinetic processes which lead to the distribution peaks. The dominant boundary by far is the one known as $B[22]$, which accounts for almost half of all observed boundaries. The atomic structure for
this type of boundary has been established as a truncated 7×7 unit cell. Thus, these boundaries are linear arrays of quasi-7×7 embedded in a sea of 5×5.

On the Si(111)7×7 surface the Group 13 elements, when deposited at sub-ML coverages and low temperatures, form magic clusters. The perfect uniformity and precise registration that earns them the moniker ‘magic’ make these clusters unusual among self-organized atomic scale objects. The clusters that form on 5×5 lack the uniformity of their counterparts on 7×7. However, with many domains, deposited In or Ga segregate to the quasi-7×7 B[22] boundaries and there form magic clusters. The boundary thus acts as a template for growing straight lines of precisely spaced, atomically identical, nanoscale clusters.
Acknowledgments

First and foremost I have to extend my thanks to my supervisor Alastair McLean, a man of inexhaustible patience.

My journey as a student began under the tutelage of one generation of fellow students, and ended under another. The skills and sense taught me by my forbears Josh Lipton-Duffin, Jenny MacLeod, and Jill Miwa have served me well, long though they have departed. The generation of students that succeeds me have been just as instructive. I have learned renewed enthusiasm from Jay Weymouth, tenacity from Ben Drevniok and the power of consideration from Will Paul. The contributions of Steve Ball, Jason Visser and Ryan Hairsine are no less. All of them have been not only good teachers, but good friends.

To the technical staff in Stirling Hall I have been a scourge. Gary Contant, Dirk Bouma, Bernie Ziomkiewicz, Steve Gillen and Kim MacKinder will all no doubt notice a steep reduction in the amount of pilfered equipment, emergency circuit diagnoses, and rush orders.

I have to thank my mother, brother, and sister for all their support. But most of all, I’m eternally grateful for the relief and reenforcement provided by my wife and son. I do not know how anyone could attempt an endeavour like this, without a foundation like them.
Statement of Originality

With the following exceptions the work presented here is that of the author, supported and guided by supervisor Alastair McLean. The exceptions are: the equations, presentation, and figures explaining STM theory presented in Ch. 2 are adapted by the author from Refs [137, 10, 184, 183, 57]. The details of the DAS reconstructions explained in Ch. 3 are well established, but the presentation is the author’s own. The microscope and vacuum systems in Ch. 4 were designed by Antje Lucas, Geoff Mullins, Jenny MacLeod and Alastair McLean, but were heavily modified by the author. The cold stage for sample cooling was designed by Jason Visser under the supervision of the author and Alastair McLean. The material in Chapter 5 is derived from Refs. [189, 190, 188, 9, 222]. The phase diagram Fig. 5.5 was constructed by the author based on the literature reports found in Table 5.1. The Germanium growth procedures outlined in Fig. 5.6 were developed by the author.

The nomenclature for the identification of DAS domain boundaries was developed independently by the author before the equivalent system by Itoh et al. [83] was uncovered. However, introducing the symmetric modulo, the prefix letter denoting the propagation direction, and the important clarifying points that remove ambiguity from the notation, were the author’s own work. The data for In clusters on Ge5×5 found at the beginning of Ch. 12 were largely derived from work done by Jenny v
MacLeod. The accompanying calculations were performed by Demetra Psiachos under the supervision of Malcolm Stott.

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<tr>
<td>AO</td>
<td>Anomalously Ordered</td>
</tr>
<tr>
<td>ACA</td>
<td>Alternating Current Amps</td>
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<tr>
<td>ARPES</td>
<td>Angle Resolved Photoemission Spectroscopy</td>
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<tr>
<td>BL</td>
<td>Bilayer</td>
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<tr>
<td>CH</td>
<td>Corner Hole</td>
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<tr>
<td>DAS</td>
<td>Dimer-Adatom-Stacking Fault</td>
</tr>
<tr>
<td>DCA</td>
<td>Direct Current Amps</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>DOS</td>
<td>Density of States</td>
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<tr>
<td>FHUC</td>
<td>Faulted Half Unit Cell</td>
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<tr>
<td>HUC</td>
<td>Half Unit Cell</td>
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<tr>
<td>LDOS</td>
<td>Local Density of States</td>
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<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
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<tr>
<td>LEEM</td>
<td>Low Energy Electron Microscopy</td>
</tr>
<tr>
<td>MEIS</td>
<td>Medium Energy Ion Scattering</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
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<tr>
<td>NO</td>
<td>Normally Ordered</td>
</tr>
<tr>
<td>PES</td>
<td>Photoemission Spectroscopy</td>
</tr>
<tr>
<td>REM</td>
<td>Reflection Electron Microscopy</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
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<tr>
<td>STS</td>
<td>Scanning Tunneling Spectroscopy</td>
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<tr>
<td>UHUC</td>
<td>Unfaulted Half Unit Cell</td>
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<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
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<td>XSW</td>
<td>Xray Standing Wave</td>
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Chapter 1

Introduction

One of the challenges facing nanoscience is the very question of how to build things on the scale of atoms. The ideal system would allow features of arbitrary atomic arrangement to be placed with atomic scale precision at positions of the designer’s choosing. Atomic manipulation using scanning probe tips approaches this ideal. However, top-down techniques like this one will always suffer from poor scalability. On the other hand, the precision and flexibility of parallelizable self-organization schemes falls well below that desired. Indeed, no self-organization scheme permits precise assembly of arbitrary designs at the atomic scale. Instead, one approach for self-organized techniques has been to pursue systems which exhibit uniformity and precision, but are not arbitrary. In these systems the objects created are atomically precise in their configuration and position, but those configurations and positions are dictated by nature rather than a designer.

Two approaches which have met with some success in this pursuit are the decoration of step edges, and magic clusters confined by surface reconstructions. In the former, the high dangling bond density and unique atomic geometry of the symmetry
breaking steps leads to the preferential nucleation of features at the step edge. In the latter, the reconstruction templates clusters of adsorbate into a pattern with a periodicity imposed by the reconstruction. In both cases careful choice of the substrate and adsorbate can improve the uniformity of the cluster features that form. The pinnacle is represented by magic clusters, which exhibit almost perfect uniformity.

Cluster growth on reconstructions leads, naturally, to a 2D array of features. Steps break the symmetry of the surface and yield 1D arrays of clusters. The approach here is to take advantage of another type of 1D surface defect to encourage linear cluster growth. That defect is the boundary found between domains of the Si(111)-Ge5×5 reconstruction.

These boundaries are interesting in their own right, and because they have been studied very little, they are ripe for investigation. For instance, and most importantly, they can be made straight and uniform. The atomic structures found at their cores reflect and reinforce the energy difference between features in the 7×7 unit cell. Furthermore their registration with the surface imposes simple and elegant rules for how they interact with one another. However, these domain boundaries, especially those of a particular type, also serve as templates for the growth of 1D arrays of magic clusters. Each cluster is identical, and the periodicity of the boundary ensures their registration with one another along a straight line.

1.1 Document Organization

This manuscript is divided into 14 chapters. The first seven are largely background. Chapter 2 reviews the theory of operation of the scanning tunneling microscope, the primary experimental tool for this work. Chapter 3 introduces the Si(111)7×7
dimer-adatom-stacking fault reconstruction, and its smaller cousin the 5×5 reconstruction which will prove particularly important here. Chapter 4 discusses some of the experimental apparatus. In particular, the microscope, sample preparation and thermometry equipment, and evaporators used to deliver adsorbate to surfaces. A complementray chapter detailing the design and performance of the sample cooling stage is found in Appx. A. An introduction to the growth of Ge is provided in Ch. 5. Chapter 6 examines magic cluster growth with special emphasis for the Group 13 metals on 7×7. Finally, Ch. 7 reviews the literature pertaining to domain boundaries of the Si(111)7×7 reconstruction.

Although most of the material presented in Ch 1–7 is review there are important sections of original work. Of particular importance are the details of sample preparation for Si(111)7×7 and Si(111)-Ge5×5 presented in Secs. 3.9 and 5.6.

Chapters 8–11 explore the domain boundaries that form on Si(111)-Ge5×5. A notation to describe these boundaries is introduced in Ch. 8, which also examines the symmetry properties of such boundaries. A complementary reference for vector math in a hexagonal basis is included as Appx. B. Chapter 9 provides a comprehensive atlas of STM images of each type of domain boundary, along with proposed atomic models. Chapter 10 investigates the relationships that exist between the domain boundaries that meet at a vertex. To that end it introduces a notation for describing boundary vertices, and provides examples of commonly observed kinks and vertices. A complete catalog of vertices can be found in Appx. C. Finally, Ch. 11 considers the connected network of boundaries on the surface collectively. It postulates evolutionary processes that might explain why the observed distribution of boundaries is dominated by a handful of the possibilities.
Chapters 12 and 13 return to magic clusters. Chapter 12 reviews and builds on earlier work growing In and Ga clusters on Ge5×5. It demonstrates and attempts to explain why cluster growth on 5×5 is not magical. Chapter 13, on the other hand, shows that the dominant domain boundary on 5×5 is effective at stabilizing and patterning identical magic clusters into 1D arrays. The concluding chapter, Ch. 14, reviews the work presented and attempts to suggest courses for future research.
Chapter 2

Theory

The basic principles of scanning tunneling microscopy are well known; a sharp metal tip is brought into close proximity with a metal or semiconducting surface and a current flows between the two, even without direct contact. Piezo elements exercise exquisite control over the position of the tip and a surface is mapped out by scanning the tip over it. The goal of this chapter is to review the origin and characteristics of the tunneling current that lies at the heart of the STM. The rudiments of 1D electron tunneling are covered in any undergraduate quantum mechanics curriculum. Here we apply those results for electron tunneling in free space to a solid state system before reviewing the contributions of Bardeen, and Tersoff and Hamann. The goal is only to draw a rough sketch of the principles at work in the microscope. In particular, what is being measured, the origins of contrast, the effect of the tip, and the limits to the assumptions that go into each of these. The material reported here is the author’s interpretation of the more detailed reviews of tunneling theory available in Ref. [57, 76].
Figure 2.1: The Finite Square Barrier. An electron impinging on the barrier from the left has a finite probability of penetrating and continuing at the right. The tunneling probability is a function of the electron’s energy, the barrier’s height and width.

2.1 The Direct Method

The classic introduction to quantum mechanical tunneling is the problem of the finite square barrier. The following analysis is patterned on one that can be found in any undergraduate quantum mechanics text, for instance Ref. [26]. The question asked is, what happens when an electron traveling from the left (Fig. 2.1) impinges upon a potential barrier of width $z_o$ and height $B$? We will call the three regions the sample, the gap, and the tip to reflect the situation in the microscope. The incoming electron has the free electron wavefunction

$$\psi(z) = e^{ikz}$$  \hspace{1cm} (2.1)
where the wave vector \( k = \sqrt{2mE/\hbar} \), and \( E \) is the electron energy. Scattering and partial reflection will occur at the sample–gap and gap–tip interfaces. The wave-function can be found exactly by using plane wave solutions for the transmitted and reflected components and ensuring that the total wavefunction and its first derivative are both continuous. The transmission coefficient, the probability that an electron approaching from the left will successfully cross the gap and make it to the other electrode, is

\[
T(E) = \left[ 1 + \frac{B^2 \sinh^2 (\kappa z_0)}{4E(B - E)} \right]^{-1} \quad (2.2)
\]

\[
\sim 16 \frac{E}{B} \left( 1 - \frac{E}{B} \right) e^{-2\kappa z_0}, \quad (2.3)
\]

where \( \kappa = \sqrt{2m(B - E)/\hbar} \) is the decay constant within the gap. The essential feature is that there is a finite probability of the electron penetrating a barrier that is classically impassable. This is the phenomenon known as tunneling. The exponential decay of transmission with gap spacing is at the heart of the STM’s extraordinary resolution.

This result can be applied to the situation where many electrons are available for tunneling so that its effect is macroscopically observable. In this case the tip and sample are metal electrodes separated by a vacuum gap. In a metal, electron states are plane waves like Eqn. 2.1 and all the states below the Fermi level are occupied, shown by the grey areas in Fig. 2.2a. When the two electrodes are in equilibrium, the Fermi levels align. In this case elastic tunneling, which most transmission events are, is forbidden since there are no unoccupied states into which to tunnel. But, if an external bias is applied, the Fermi levels shift relative to one another and there
is now a range of occupied states in the sample (shown by the dark region) which corresponds to unoccupied states in the tip. The states in this window are available for tunneling. On the other hand, no energetically accessible states are available for tunneling from tip to the sample. Experimentally, this net imbalance of electron tunneling is measured as an electrical current. The situation presented here, where the sample is biased positive with respect to the tip, is known as filled state imaging. If the bias is applied in the opposite sense, electrons will tunnel from the tip into unoccupied states in the sample. This is empty state imaging. If $V$ is small then the distortion to the tunneling barrier will be small and Eqn. 2.3 will remain approximately valid. In this case, the contribution to the current of one state of energy $E_n$ is proportional to

$$I_n \propto ev_n T(E_n) = e\sqrt{2mE_n} T(E_n),$$  \hspace{1cm} (2.4)$$

where the electron velocity $v_n = \sqrt{2mE_n}$ for a free electron metal. The total current
is the sum over all the participating states in the sample

\[ I \propto e \sum_{E=E_F-eV}^{E_F} \sqrt{2mE_n} T(E_n). \] (2.5)

Furthermore, for small \( V \), the sum is restricted to energies near \( E_F \), so \( T(E_n) \approx T(E_F) \) and

\[ I \sim e \sqrt{2mE_F} T(E_F) \sum_{E_n=E_F-eV}^{E_F} 1. \] (2.6)

The sum now simply represents the number of states in the sample between \( E_F \) and \( E_F - eV \). When \( V \) is small this can be replaced with the density of states \( \rho_{\text{sam}}(E_F) \) at the Fermi level times the width of the energy window for tunneling \( eV \). Writing the barrier height in terms of the work function \( \phi = B - E_F \), the current is

\[ I = e^2 \sqrt{2mE_F} T(E_F) V \rho_{\text{sam}}(E_F) \] (2.7)

\[ = 16e^2 V \rho_{\text{sam}}(E_F) \sqrt{2mE_F} \frac{E_F \phi}{(E_F + \phi)^2} e^{-2\kappa z_o} \] (2.8)

\[ \propto V \rho_{\text{sam}}(E_F) e^{-2\kappa z_o}, \] (2.9)

with \( \kappa = \sqrt{2m\phi}/\hbar \). Thus, the current is proportional to \( V \), the applied voltage, and \( \rho_{\text{sam}}(E_F) \), the density of states in the sample at the Fermi level.

For this simple situation, the solution Eqn. 2.2 is straightforward and exact (although there are several approximations in Eqn. 2.9). However, the algorithm which generated it, often called the direct method, becomes intractable when applied to three dimensional systems with physically realistic potentials. In general, for real condensed matter systems it is hard enough to calculate the sample’s band structure even without the presence of the tip. The techniques presented in the following
sections were devised to address this concern, but almost all of the important characteristics of tunneling in the STM are already present in Eqn. 2.9: the exponential decay with gap spacing, the ohmic behavior for metals at small bias, and the dependence on the density of states. The important missing piece is the lateral sensitivity, the very thing that makes STM so useful.

### 2.2 Tersoff and Hamann

The solution to the difficulties in applying the direct method to realistic potentials is to mathematically decouple the tip and sample from one another. This was first done by Oppenheimer in the context of field ionization of atomic hydrogen [137]. His approach ultimately came down to calculating the matrix elements connecting sample states $\psi_k$ to tip states $\chi_j$

$$M_{\psi_k\chi_j} = \langle \chi_j | H - H_{sam} | \psi_k \rangle [137]. \tag{2.10}$$

Once that is done the tunneling current is

$$I = \frac{2\pi e}{h} \sum_k \sum_j |M_{\psi_k\chi_j}|^2 \delta(E_j - \varepsilon_k)[f(E_F + eV - \varepsilon_k) - f(E_j - E_F)][184]. \tag{2.11}$$

Here the sum is over all states, but the term $\delta(E_j - \varepsilon_k)$, where $E_j$ is the tip state energy and $\varepsilon_k$ is the sample state energy, enforces elastic tunneling. The Fermi-Dirac distributions $f(E)$ ensure that tunneling only occurs from occupied states into unoccupied ones.

Bardeen’s contribution was to find a more symmetric way to write the matrix
elements, one which doesn’t require returning to the original Hamiltonians and relies only on the wavefunctions themselves [10]. His famous transfer Hamiltonian,

\[ M_{\chi\psi} = \frac{-\hbar^2}{2m} \int_{\partial T} \left[ \chi^* \nabla \psi - \psi \nabla \chi^* \right] \, dn \tag{2.12} \]

calculates the matrix elements based on an integral over a surface \( \partial T \) that separates the tip and the sample.

Tersoff and Hamman (T-H) were the first to apply the transfer Hamiltonian to the STM and use it to make estimates of microscope resolution. The essential difference from the case considered by Bardeen is that the geometry is no longer planar. As a crude demonstration they began by representing the tip by a single delta-function wavefunction at point \( r_o \). This represents the limit of an infinitesimally small probe. The matrix element can be found directly from Eqn. 2.10, bypassing the transfer Hamiltonian [184]

\[ M_{\delta \psi} = \int \delta(r - r_0) [H - H_{sam}] \psi_n \, dr \tag{2.13} \]

\[ = \int \delta(r - r_0) H \psi_n \, dr \tag{2.14} \]

\[ = H \psi_n(r_0) \tag{2.15} \]

\[ |M_{\delta \psi_n}|^2 \propto |\psi_n(r_0)|^2 \tag{2.16} \]

and the tunneling current, from Eqn. 2.11, is [184]

\[ I \propto \sum_n |\psi_n(r_0)|^2 \delta(\varepsilon_n - E_F) = \rho_{sam}(r_0, E_F). \tag{2.17} \]

The function \( \rho_{sam}(r, E) \) is known as the local density of states (LDOS), and a tip with
a point-like wavefunction measures the LDOS at the position of the tip and at the Fermi energy. So an STM maps out contours of LDOS in three dimensional space.

A more realistic model is to take the tip potential as a spherically symmetric well of radius $R$. In this case the radially symmetric tip wavefunction when $r >> R$ is $\chi_j \sim A_j e^{-k_j r}/r$. Since it lacks angular dependance, this is known as the $s$-wave approximation. It predicts a tunneling current, in the limit of low bias and zero temperature, of

$$I = \frac{8\pi^3 \hbar^3 e^2}{m^2} \rho_{\text{tip}}(E_F) R^2 e^{2\kappa R} \rho_{\text{sam}}(r, E_F)$$

(2.18)

Here the $z$ dependance of tunneling current is contained within the sample density of states, which decays evanescently into the vacuum.

### 2.3 Modes of Operation

The various expressions for tunneling current (Eqns. 2.11, and 2.18) suggest several different modes for operating an STM, each of which measures a different physical quantity. The first two techniques are spectroscopic. In the first the bias and lateral position are fixed, and the current is measured as the tip approaches the sample. Since $\ln I = c - 2\kappa z$ this is a measurement of the decay constant $\kappa$ and hence the height of the tunneling barrier. Measurements of this type were the first reported by Binnig & Rohrer from their infant STM [22]. In the second measurement mode, the tip is held at a fixed position, and the tunneling current is measured as the sample bias $V$ is ramped. As the bias increases more states become available for tunneling, and the current increases. The rate at which it increases, $dI/dV$ is a measure of the
DOS at the bias $V$, so this measurement is known as scanning tunneling spectroscopy (STS).

The last two modes of operation are imaging techniques where the tip is scanned in $x$ and $y$ over the surface and generates a two dimensional map. In constant height operation the tip height $z$, and bias voltage are fixed and the current is measured. The resulting image maps the current at height $z$, at each point $x$, $y$ in the frame. In constant current mode the tip height is modulated with a feedback loop to maintain a fixed tunneling current even as the tip is rastered over the surface. Images produced in this mode are isosurfaces of LDOS. Virtually all STM images reported in the literature (and this is true of the images presented here) are constant current images. This ubiquity is for practical reasons: constant height mode risks the tip crashing into protrusions in the scan area. In constant current mode the feedback loop will protect the tip by ensuring a constant separation between the tip and the surface.

### 2.4 STM Resolution

Tersoff and Hammon demonstrated the resolution of the STM by examining a 2D model surface in $x, z$ where the density of states at $E_F$ is defined by two components

$$\rho(x, z) = \rho_0(z) + 2\rho_{g_1}(z) \cos(g_1 x).$$  \hspace{1cm} (2.19)

The first component is constant in $x$, but decays into the vacuum ($z > 0$). The second term decays into the vacuum, but also varies sinusoidally with lateral position, and has a period reflected by the reciprocal lattice vector $g_1$. The contribution from the
Brillouin zone centre ($g = 0$) has a decay profile like the one in Eqn. 2.3

$$\rho_0(z) \propto \exp(-2\kappa z). \quad (2.20)$$

On the other hand, $\rho_{g_1}$ decays into the vacuum as

$$\rho_{g_1} \propto \exp\left(-2\sqrt{\kappa^2 + \left(\frac{1}{2}g_1\right)^2} z\right) \quad (2.21)$$

$$\sim \exp\left(-2\left[\kappa + \frac{1}{8}\frac{g_1^2}{\kappa}\right] z\right). \quad (2.22)$$

Once combined, they yield the local density of states

$$\rho(x, z) \propto e^{-2\kappa z}(1 + 2\cos(g_1 x)e^{-2\delta z}), \quad (2.23)$$

where $\delta = \frac{g_1^2}{8\kappa}$. Most scanning is performed in constant current mode, but for simplicity, first examine what happens when a tip is engaged in constant height scanning (i.e. constant $z$). In this mode the tip will experience the highest current when $\cos(g_1 x_+) = +1$, and lowest when $\cos(g_1 x_-) = -1$. The corresponding currents are

$$I_\pm \propto e^{-2\kappa z}(1 \pm 2e^{-2\delta z}). \quad (2.24)$$

The STM’s practical utility comes from its ability to distinguish, over atomic scale distances, the areas of high current from low current. One measure of this is the image contrast, given by

$$\chi = \frac{I_+ - I_-}{I_+ + I_-} = 2e^{-2\delta z}. \quad (2.25)$$
Figure 2.3: Tip Radius. a) The effect of tip radius on tip height required to maintain a fixed $I$ at a given $V$. b) Profiles of current taken at different constant tip heights. As $z$ increases the corrugation decreases.

High contrast (large $\mathcal{X}$) means that the high current at $x_+$ is easily discerned from the low current at $x_-$. In this case, since $\delta > 0$, contrast diminishes rapidly with increasing $z$. Note that the contrast dwindles because of the $\exp(-2\delta z)$ factor applied to the sinusoidal term in $\rho_q$. This is precisely the effect of applying a Gaussian convolution with full width at half maximum of $2\sqrt{\ln(2z/\kappa)}$ [184]. So, one perspective is that the contrast drops because higher $z$ scanning results in a wider Gaussian convolution — the microscope’s resolution decreases with height.

Turn now to the effect of tip radius. For a given average current $\bar{I} = \frac{1}{2}(I_+ + I_-)$ and bias voltage $V$, the height $z$ increases quickly with $R$ since $I \propto R^2 \exp(2\kappa R)$. Since the resolution decreases with height, the net result is that larger tip radii result in degraded contrast. More precisely, the contrast change with tip radius is

$$\frac{d\mathcal{X}}{dR} = \frac{\partial \mathcal{X}}{\partial z} \left( -\frac{\partial \bar{I}/\partial R}{\partial \bar{I}/\partial z} \right)$$

$$\sim -2\delta \left( 1 + \frac{1}{R\kappa} \right) e^{-2\delta z}. \quad (2.26)$$
This is always negative. So sharper tips, unsurprisingly, give improved contrast.

## 2.5 Numerical Example

A numerical example is a useful exercise in not only demonstrating the strengths, but also the deficiencies of the $s$-wave model. For Au(100) the work function $W = 5.5$ eV [55], so the decay constant $\kappa = 1.2 \text{Å}^{-1}$. The smallest surface reciprocal lattice vector is $g_1 = 2\sqrt{2}\pi/a_o \sim 2.2 \text{Å}^{-1}$, and the density of states at the Fermi level is $\rho_{\text{sam}} = \frac{3}{2} \bar{n}/E_F = 0.016 \text{Å}^{-1} \text{eV}^{-1}$. The effective radius for an ideal tip consisting of a single W atom is roughly twice the inverse decay length $R \sim 2\kappa_W^{-1} \sim 1.82 \text{Å}$.

Combining these gives an average tunneling current at $10 \text{mV}$ of

$$I \sim 2 \text{mA} \cdot e^{-1.2 \text{Å}^{-1}z}. \quad (2.28)$$

To maintain a tunneling current of $1 \text{nA}$, typical for STM, the tip height must be $z = 6.1 \text{Å}$. Increasing the distance by $30\%$ to $8 \text{Å}$ decreases the current by one-hundredfold, to $10 \text{pA}$. Doing so increases the resolution width from $3.75 \text{Å}$ to $4.3 \text{Å}$ and decreases the contrast from $4 \times 10^{-3}$ to $8 \times 10^{-4}$. On the other hand, if the tip radius doubles then to maintain an average current of $1 \text{nA}$ at $10 \text{mV}$ requires that the tip be pulled back to $z = 8.5 \text{Å}$, where the contrast drops to $\sim 4 \times 10^{-4}$, and the resolution is $4.4 \text{Å}$.

These values highlight the primary failure of the $s$-wave model: it does not predict atomic resolution. According to the model, to achieve a resolution of $2 \text{Å}$, which gives a now useful contrast of 0.4, requires the tip be positioned at $z = 1.7 \text{Å}$, with an effective radius of $\sim 8 \text{pm}$. Clearly, this is unrealistically small. The origin of the higher resolutions experienced in practice will be explained in the next section.
2.6 Limitations

The preceding arguments give a compelling description of the operation of an STM. However, each of the key features have limits to their validity thanks to the assumptions used to arrive at them. This section attempts to point out some of the ways in which real scanning diverges from the simplified schematic vision outlined so far.

The analyses presented above all assume that tunneling is a single electron event. In cases where electron–electron, electron–phonon, or charging effects are important the tunneling characteristics will change considerably. It is also assumed that the wavefunction overlap between tip and sample states is small. This is the weak tunneling regime, and for metals it is reasonable when the separation is larger than \( \sim 5 \text{ Å} \) \cite{76}. At shorter distances chemical bonds between the tip and surface lead to distortion of the atomic positions, in which case the tip and surface — and thus their wavefunctions — no longer resemble their forms in isolation. When that happens tunneling can only be realistically modeled using a more advanced formalism (like the Landauer-Bütticker or Keldysh-Green’s function approaches \cite{76}) that treats the sample–gap–tip system in its entirety.

Perhaps the most important feature of the tunneling current is that it is a measure of the sample local density of states. So to put it crudely, STM images are pictures of electrons, but not of nuclei. In fact, in many cases atoms which share the same true vertical height have dramatically different apparent heights in STM images because of different local environments, and hence local densities of states. This is true, for instance, of the adatoms in the Si(111)7×7 reconstruction. Based on LEED \cite{185} and dedicated \textit{ab initio} calculations \cite{90} the ion positions of the corner adatoms in the faulted and unfaulted halves are known to differ in height by \( \sim 0.08 \text{ Å} \). But in
CHAPTER 2. THEORY

filled state STM images the apparent height difference can be \( > 0.3 \text{Å} \)[90, 64]. The electronic properties of the reconstruction, and the implications for STM images, will be discussed more fully in Ch. 3. In extreme cases corrugation inversion occurs and the atomic positions appear lower than the areas between them [11, 34].

The tip enters Eqn. 2.18 in two ways: through its effective radius \( R \), and its density of states \( \rho_t(E) \). The idea that these two effects are decoupled, and that changes to the tip’s radius have no effect on the density of states, is itself a construct, but a useful one that will be continued. It has already been seen that the \( s \)-wave model does not predict atomic resolution. Yet, resolving individual atoms, and even sub-atomic features [69], is regularly achieved. This discrepancy arises because of the broad spherically symmetric \( s \)-wave tip used in the approximation. Chen pointed out that \( d_{z^2} \) orbitals are found at the surface of W. These states have strong angular dependence, and are more confined laterally than the \( s \)-wave orbitals used in the estimate, and consequently lead to higher resolution [33]. Chen’s analytic extension to Tersoff and Hamann’s formulation for the tunneling current does indeed predict corrugation amplitudes comparable to those observed. In general, the true tip wavefunction will be a function of the chemical species, and the local environment of the tip apex, factors which are never known (except in the most meticulous experiments [110]).

The other influence of the tip is through its density of states. In our numerical estimates we used the density of states for W, assuming free electron behaviour. In reality, like the spatial profile of the tip wavefunction, the density of states will depend in a complicated way on the chemical species and apex geometry. This modifies the tunneling current by a constant prefactor. However, since the same tip is used to scan
Figure 2.4: Preferred Tunneling. Higher lying states have a lower tunneling barrier and thus higher tunneling probability. a) For positive bias, these preferred states are just below the tip Fermi level. If the tip LDOS is flat the tunneling current reflects the LDOS of the sample at $V$. b) For negative bias, the preferred states are just below the sample Fermi level; tunneling current reflects the LDOS of the sample at $E_F$ regardless of $V$.

the entire surface, if the tip is sharp enough differences in the sample LDOS—the point of the exercise—will be faithfully reproduced in the current contrast, regardless of the details of the tip apex. On the other hand, that constant prefactor will vary in energy differently for different tip configurations. So scanning tunneling spectroscopy (measuring $I(V)$ at constant $z$ and position) is sensitive to the tip details. This has been taken to an experimental extreme by using semiconductor tips whose bandgaps permit tunneling only within a narrow and well-understood window [174].

We have already mentioned the technique of scanning tunneling spectroscopy, where the sample bias is swept through a range of voltages and, with tip position fixed, the current is monitored. As the window of energetically allowed tunneling widens the current increases. For metals at small biases the density of states near the Fermi level is relatively constant and so the linear approximation in Eqn. 2.18 is
reasonable. At large biases, or on semiconducting samples, $I-V$ profiles do reflect the sample density of states (assuming constant tip DOS), but are complicated by the details of tunneling [76, 130].

The most important consideration is that tunneling is an asymmetric process, and tunneling from the tip to sample is different than the other way around. Electrons in higher lying bands are closer to the vacuum level, and thus have a smaller barrier to penetrate than those at lower energies. Electrons at the Fermi level have the smallest barrier, $\sim \phi$, of all. Since the tunneling probability has an exponential dependance on the barrier height electrons at the Fermi energy will be much more likely to tunnel than those lower. For positive bias the tunneling current will be dominated by tunneling into sample states at energy $+V$, and will vary, in response to the changing sample LDOS, as $V$ is adjusted. On the other hand tunneling at negative bias is dominated by electrons at the sample Fermi energy. If the tip DOS is flat, then the current will not change substantially with bias. The effect is that positive bias scanning follows the sample LDOS at the selected bias, while negative bias scanning reflects the sample LDOS at the Fermi energy [18, 174].

Another important consideration is the momentum resolution of the tip. The energy of the tunneling states is controlled with the bias voltage, from where in the Brillouin zone do the electrons come? If we assume that the microsocope has a lateral resolution of $\Delta x \sim 2\text{"A}$ then the uncertainty principle restricts the precision of the tunneling electron’s in-plane momentum [174, 203] to

$$\Delta k_{||} \sim \frac{1}{2\Delta x}. \quad (2.29)$$

This is $\sim 0.25\text{"A}^{-1}$. For comparison, consider the point $K_{1x1}$, lies on the surface
Brillouin zone boundary for Si(111)1×1. This is the most distant point in the repeating zone scheme and it lies $k_\parallel = 1.09\AA^{-1}$ from the zone centre. So, for a 1×1 cell the STM only samples $k_\parallel$ states close to $\bar{\Gamma}$. On the other hand, for Si(111)7×7 $\bar{K}_{7\times7} = 0.16\AA^{-1}$, well inside the range of $\Delta k_\parallel$: the microscope samples the entire Brillouin 7×7 zone. Thus, bands which disperse with the periodicity of 7×7 resolve broadly in STS.

Real scanning is always done at finite temperature, rather than the $T = 0$ approximation. The first effect of finite temperature is to broaden the Fermi function which leaves some states above the Fermi energy occupied and some states below unoccupied. This increases the energy uncertainty of the applied bias, and broadens the microscope’s energy resolution. However, finite temperature has an important effect on the structure of what is being observed, by exciting higher energy structural configurations of the surface, beyond the ground state structure. The clearest example of this are the dimers on Si(100). At low temperatures the surface adopts a c4×2 configuration with alternating buckled dimers [205]. At higher temperatures there is enough energy for dimers to overcome the barrier to flipping, and they alternate between the two buckled orientations. Since the frequency of flipping is higher than the STM scan rate, images at $> 90$ K show flat dimers with a 2×1 appearance [63, 66]. This illustrates two points: first, higher temperatures allow the surface to explore configurations that are kinetically forbidden at lower temperatures. Secondly, the STM can be fooled by rapid conformational changes: in the case of Si(100)2×1 the dimers appear flat, but are actually always buckled, the microscope sees the average of the two configurations.
2.7 Summary

The theory of tunneling in the STM has been reviewed from Oppenheimer to Bardeen, and on to Tersoff and Hamann. Much of the flavour of these later theories is neatly captured in the expression for tunneling theory solved using the direct method. The important points are that the tunneling current

- measures the sample’s local density of states at the position of the tip centre

- is modulated by the tip density of states

- increases with voltage in a way that reflects the sample density of states

- has lateral resolution that falls off with increasing tip radius
Chapter 3

The DAS Reconstruction

This chapter will serve to introduce the concept of reconstruction and will delve into the details of the famous Si(111)7×7 dimer adatom stacking-fault (DAS) reconstruction. The geometry of the reconstruction will be examined, as will its electronic structure, and the forces driving its formation. The opening material is established as received knowledge in the field. However, the final section, provides details of the experimental procedures that were developed and used by the author.

3.1 Relaxation, Reconstruction and Wood’s Notation

An atom within a crystal is subjected to forces in all three dimensions from its neighbours. In equilibrium, these forces are balanced, and, below the melting temperature, the atom does not move far from the equilibrium position. When a surface is formed, the forces on the newly exposed atoms will no longer be balanced and the atoms will
move to new equilibrium positions. These new locations are sensitive to the nature of bonding for the material. The different responses, shown in Fig. 3.1, are known as ideal, relaxed, and reconstructed.

A surface for which the surface atoms do not move from their bulk terminated positions is called ideal. Such surfaces are hypothetical and serve only as an archetype against which real surfaces are compared. Metals, for which bonding is largely isotropic, often respond to a surface through relaxation: the exposed surface layer moves into or away from the surface, but the lateral symmetry of the surface is unchanged [222].

Semiconductors, on the other hand, have strong directional bonds and the new surface structure is dictated by the surface atoms’ desire to complete the bonds that were broken when the crystal was cleaved. This results in atomic movements both in and out of the plane. This conformational change is known as reconstruction [222, 189]. Although the reconstruction unit cell is generally larger than the ideal unit cell, it will be commensurate, and thus can be described in terms of the ideal lattice. The most general notation for describing a reconstruction is the matrix notation introduced by Park and Madden [141]. However, in cases where the angle between the two basis vectors is unchanged from the ideal the simplified Wood’s notation is used [206]. In this case, a general surface reconstruction on the \((hkl)\) face of crystal \(X\) is expressed in Wood’s notation as

\[
X(hkl)m \times n\mathbf{R} \phi.
\]

The second term indicates that the reconstruction unit cell is \(m \times n\) times the ideal one. The \(\mathbf{R}\) indicates that the reconstruction unit cell is rotated by angle \(\phi\) relative to the
Figure 3.1: Ideal, Relaxed, and Reconstructed Surfaces. A schematic showing three possible outcomes from cleaving a simple cubic crystal. The top half of each panel shows a plan view of the surface and the bottom half shows a side view. The top layer atoms are drawn as open circles for clarity. The shading does not indicate a chemical difference.

a) An ideal surface where the exposed atoms show no change from their bulk crystalline positions. b) In relaxation, the top few layers sink closer to those below. c) Reconstruction: the atoms of the first layer have rearranged to form dimers. The result is a surface which has periodicity of $2 \times$ the ideal surface in the $a_1$ direction and $1 \times$ in the $a_2$ direction. This is a $2 \times 1 \times$ reconstruction.

ideal cell. In the absence of rotation the $R\phi$ is omitted. Reconstructions expressed such are primitive. Sometimes a ‘$p$’ is added to contrast against the case where the unit cell is centred, which is expressed $c(m \times n)$. Centred cases arise when the middle structural unit of the reconstruction unit cell is crystallographically identical to the ones at its perimeter. Wood’s notation is simply a description of the size and orientation of the reconstruction unit cell with respect to the underlying substrate, it does not reveal the internal structure or symmetry of the unit cell.
3.2 Bulk Silicon

Bulk silicon has the diamond crystal structure which consists of two interpenetrating fcc lattices. Fcc itself can be imagined as a close-packed arrangement of equilateral triangle (111) planes with the stacking sequence ...ABCABC... [7, p79]. The nearest neighbour spacing between the atoms in the triangles is $a$, for Si(111) this is 3.84 Å. Each atomic plane is shifted by $\frac{1}{3}a$ in the [11\bar{2}] direction relative to the plane below. The basis in diamond means, as shown in Fig. 3.2, that for every layer of fcc another basis layer is added. The sequence becomes one of pairs known as bilayers (BL) ...AaBbCcAaBbCc... The shift between A and a is again $\frac{1}{3}a$ in the [11\bar{2}] direction, so the atoms in the bottom of each bilayer lie directly above the atoms in the top of the bilayer below. Bulk silicon adopts this structure because it permits Si’s preferred tetrahedral bonding geometry. Each Si atom is bonded to four nearest neighbours with bond angles of 109.5°. Three bonds are with atoms in the other half of the same bilayer and one bond is with the next bilayer.

3.3 Ideal Si(111)

When it comes to form a surface, the planar cut can be made between bilayers (...AaBb) or within a bilayer (...AaB). The former breaks one bond per unit cell, the latter breaks three. Thus, the Si(111) surface is always terminated by a complete bilayer. This is observed in cleaving for which the inter-bilayer cut is the one always seen [48, 45], and growth where new islands are organized by bilayer [193]. The crystallographic directions on the Si(111) surface are shown in Fig. 3.3. Note that because of the bilayer stacking sequence reciprocal directions are inequivalent.
Figure 3.2: The structure of ideal, bulk-terminated Si(111). The top panel shows the surface viewed from the top, and the bottom shows it from the side. The unit cell is shown at the bottom left. The unit vectors $a_1$ and $a_2$ are the unit vectors of the ideal $1 \times 1$ cell against which all reconstructions are measured. The diamond stacking sequence ...AaBbCc is illustrated with the coloured triangles near the right and their corresponding side views below. In the top view, they have been shifted for clarity. The standard site labels are depicted on the unit cell near the upper left and described in the table below.

<table>
<thead>
<tr>
<th>$T_1$</th>
<th>Atop a top layer site</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_4$</td>
<td>Atop a second layer site</td>
</tr>
<tr>
<td>$B_2$</td>
<td>Bridge, halfway between two top layer sites</td>
</tr>
<tr>
<td>$H_3$</td>
<td>Threefold hollow above second bilayer site</td>
</tr>
<tr>
<td>$B_1$</td>
<td>Midway between $T_1$ and $H_3$</td>
</tr>
</tbody>
</table>
The ideal Si(111)1×1 surface, which is never observed, is shown in Fig. 3.2. The unit cell is defined by the dark diamond which measures $a = 3.84 \, \text{Å}$ on each side. Several locations in the ideal 1×1 unit cell possess high symmetry and have acquired special names which are labeled in the figure, and compiled in the table below Fig. 3.2 [16, p154].
3.4 Si(111) 7×7

Every unit cell of the bulk terminated Si(111)1×1 surface contains one surface atom with a single dangling bond pointing along the surface normal. This is a very high dangling bond density (1 dangling bond per 1×1 UC) and it always leads to reconstruction. At room temperature the cleaved structure reconstructs into a 2×1 structure [140, 47]. However, this is a metastable phase. Upon annealing to 850° C, the surface irreversibly changes into a 7×7 reconstruction. This was first observed by Schlier and Farnsworth in 1959 [163], but for thirty years the huge unit cell defied
Table 3.1: Breakdown of atoms in the $7 \times 7$ reconstruction.

precise specification of the atomic arrangement. It was not until 1985 when, assisted by results from the recently introduced STM [21], Takayanagi’s careful transmission electron diffraction analysis finally unlocked the structure of $7 \times 7$ [179]. The reconstruction represents a delicate balance between the energy gain that comes from completing bonds versus the cost of strain from deviating from the bond lengths and angles found in the bulk.

A schematic of Takayanagi’s structure is shown in Fig. 3.4. It consists of three layers of reconstructed Si built upon an essentially ideal bulk foundation. The unit cell is divided into two triangular half unit cells (HUCs) that are distinguished from one another by the presence and absence of a stacking fault. The names of the layers are derived from their most prominent feature; from the top down they are known as the adatom layer, restlayer (sometimes stacking fault layer) and the dimer layer. The reconstruction is known as a dimer adatom stacking-fault (DAS) reconstruction after these features. There are 102 atoms in the top three layers of the reconstruction. If the upper bilayer of bulk is included the number grows to 200. Of those, 37 are unique, related to the others by symmetry [28]. They can be broken into nine broad
categories as shown in Table 3.1, and shown in Fig. 3.4.

In the following a superficial description is given of the characteristics of each type of constituent atom. The model in Fig. 3.4 and the descriptions that follow are schematic; they use an idealized geometry based bulk Si positions. This is sufficient for the purposes of the work presented here. But in reality the atoms in the reconstruction exhibit small deviations from this idealized geometry. These have been determined with high precision by low energy electron diffraction (LEED) [185] and by ab initio calculations [90, 172]. In aggregate there is a net 0.6% increase in bond lengths over the bulk value.

### 3.4.1 The Bulk

There are 49 top layer bulk atoms, shown as black filled circles in Fig. 3.4, each with a bond pointing along the surface normal. Mostly they are unperturbed from their ideal bulk positions. All but one are bonded to the dimer layer above, and thus fully saturated. The single unsaturated atom lies at the bottom of a deep void in the corner of the unit cell known as the corner hole. This depression is characteristic of 7×7 in STM images.

### 3.4.2 Dimer Layer

The dimer layer contains two distinct types of atoms, those that have formed dimers, from which the layer takes its name, and those in the HUC interior.
CHAPTER 3. THE DAS RECONSTRUCTION

Dimers

Each half unit cell is ringed by rows of dimers running in the \( \langle 10 \rangle \) directions (\( \langle \overline{1}10 \rangle \) in terms of the bulk crystal), shown by pairs of open red circles with connecting lines. They define what are often called the “short diagonals” of the unit cell. Each atom in a dimer has one bond to the bulk below, one to its pair in the dimer, and one to each of the restlayer atoms in the adjacent FHUC and UHUC.

Interior

Each of the interior atoms (individual open red circles) in the dimer layer is bonded near the ideal tetrahedral geometry to one bulk atom below and three stacking fault atoms above.

3.4.3 Restlayer

The diamond bilayer stacking sequence means that the exposed surface of ideal Si(111) does not possess mirror symmetry for reflections in the edges of the unit cell. However, the selvedge layer of the 7×7 reconstruction does. This is accomplished by introducing a stacking fault into one of the HUCs. In the unfaulted HUC the bottom bulk, top bulk, dimer layer, restlayer stacking sequence has the normal \( \ldots AaBb \) order. However, for the faulted HUC the sequence is \( \ldots AaB/c \). As a result, the sense of the three restlayer atoms supporting the adatoms is reversed from faulted to unfaulted HUC.
Restlayer Atoms

These atoms (solid blue) are fully coordinated, with three bonds to the dimer layer atoms below, and one to the adatoms above. Each adatom is supported by three such restlayer atoms.

Restatoms

Each half unit cell includes three restatoms (solid blue embossed with “R”) that differ from the others because they are not capped by an adatom, but instead carry a single dangling bond. The local geometry of each restatom is very similar to the geometry of an exposed atom of the ideal Si(111) surface.

3.4.4 Adatom Layer

There are six adatoms (solid green) in each half unit cell. Every adatom is at a $T_4$ site bonded to three restlayer atoms below, leaving a single upwards pointing dangling bond unsaturated. Within each HUC the adatoms have a $2 \times 2$ arrangement. The adatoms nearest the corner holes are distinct from those between and they are called corner and edge adatoms respectively. The corner adatoms form a six adatom ring around the corner hole.

3.5 Symmetry of the DAS Reconstruction

There are 17 2D space groups which cover the symmetries of all 2D space filling tilings. The group of symmetries possessed by the DAS reconstructions, and the ideal bulk-terminated Si(111) surface, is $p3m1$. Its members are
Figure 3.5: Symmetries of DAS. The three symmetry operations $120^\circ$ rotation, reflection, and glide reflection are shown in the legend. The grey triangle indicates the fundamental domain. The wallpaper group is $p3m1$.

- the identity

- translation by integer linear combinations of the unit vectors

- $120^\circ$ rotation about the corner holes

- $120^\circ$ rotation about the centre of the UHUC

- $120^\circ$ rotation about the centre of the FHUC

- reflection in the long diagonal of the unit cell; this is the only point symmetry operation for a single unit cell in isolation

- glide reflection along lines halfway between the nearest parallel reflection axes

The fundamental domain, the smallest area of the unit cell that will build the complete unit cell through successive symmetry operations, encloses the triangle bounded
Figure 3.6: The Symmetries of the DAS Selvedge. When the bulk below is not considered, the selvedge layer of $7\times7$ gains new symmetries. The wallpaper group is now $p6m$.

by a corner hole, FHUC centre, and UHUC centre, 1/6 the area of the entire unit cell. The fundamental contains 37 atoms in the top four layers of the reconstruction. Every one of the remaining 65 atoms in the unit cell can be related to one of these 37 by a symmetry operation that the cell diagram illustrates explicitly. If only the selvedge layers of the reconstruction are examined, and the bulk is ignored, the symmetry breaking stacking fault disappears. In this case the reconstruction’s symmetries, illustrated in Fig. 3.6, are:

- the identity
- translation by integer linear combinations of the unit vectors
- $60^\circ$ rotation about the corner holes
- $120^\circ$ rotation about the centres of the HUC
• 180° rotation about the midpoints of the unit cell edges

• reflection in the long diagonal of the unit cell

• reflection in the short diagonal of the unit cell

• glide reflection along lines halfway between the nearest parallel reflection axes.

This is space group $p6m$. The fundamental domain is now even smaller: the triangle bounded by a corner hole, the HUC centre, and half the centre of the middle dimer.

### 3.6 Electronic Structure

The first step in exploring the band structure of 7×7 is to examine the dangling bonds left exposed by the reconstruction. There are 19 in total, associated with the 12 adatoms, 6 restatoms, and one corner hole. The reconstruction lowers the total dangling bond density from the ideal case of $1/1 \times 1$ to $0.388/1 \times 1$. The remaining dangling bonds can be further subdivided based on their local geometry. Restatoms fall into two groups of three, based on whether they are in the faulted or unfaulted HUC. Adatoms fall into four groups of three: corner and edge adatoms in the faulted and unfaulted HUC. This makes for a total of 7 distinct types of dangling bonds. Associated with each of these 19 dangling bonds is an electron band. Considered independently in a tight-binding picture, each of the seven unique atom types will have associated with it a separate band with degenerate subbands. As it turns out, the bands derived from the restatom and corner hole dangling bonds are almost degenerate and have an energy well below the Fermi level [187]. Thus, charge transfer
takes place and electrons from the adatoms fully populate the $7 \times 7$ restatom and corner hole states. The remaining 5 electrons are distributed over the adatom states. Since this is an odd number, the surface is expected to be metallic. In reality the picture of isolated orbitals is too extreme, the surface states on $7 \times 7$ are delocalized and possess finite, although small, bandwidth.

Experimentally, the band structure of $7 \times 7$ has been investigated with angle resolved photoemission spectroscopy (ARPES) [157, 40, 187, 107], $k$-resolved inverse photoemission spectroscopy (KRIPE [75, 131, 74], electron energy loss spectroscopy (EELS) [40, 101] and scanning tunneling spectroscopy [64, 64, 174, 125].

**Restatoms States**

So far as the restatom states are concerned, experiments and calculations support the simple degenerate picture of $7 \times 7$’s electronic structure. The restatom states are associated with a surface band conventionally labeled $S_2$, found at $\bar{\Gamma}$ at -0.87 eV (all energies relative to the Fermi energy $E_F$) [107, 187, 118]. The band identification stems from ARPES polarization dependance $S_1$ which shows the $p_z$ character expected of restatom dangling bonds [107], and spatial localization from STM [64, 125, 174]. ARPES measurements show a band dispersion of 0.16 eV upwards from $\bar{\Gamma}$ [187, 107], which demonstrates that the band is not strictly localized. The asymmetric lineshape indicates that it contains subbands that, as yet, remain unresolved [107]. This is in accord with calculations that place the six restatom subbands in a tight, weakly dispersing manifold at -0.8 eV [138, 139, 27, 150]. Calculations report no appreciable asymmetry to the restatom dangling bonds in the faulted vs. unfaulted HUCs [27]. However, STM measurements in both CITS mode and $dI/dV$ mode show a distinct
difference in intensity between the two halves, with the FHUC being brighter [144, 125, 178].

**Corner Hole States**

In photoemission experiments, the corner hole band is presumed to be mixed, and indistinguishable, with the restatom band $S_2$ [187, 107]. This assignment is based on evidence from the seminal STM spectroscopy work by Hamers *et al.* where strong LDOS intensity over the corner holes was observed at $\sim-0.8\,\text{eV}$ [64]. However, more modern studies do not show corner hole intensity at any bias within the gap [144, 178, 125]. This absence may be caused more by the depth of the hole, and difficulty in imaging, than a true lack of electron density.

In contrast, most calculations do not predict the corner hole band to be degenerate with the restatom bands. Most, like Ortega *et al.*, predict an energy for the corner hole band of $\sim0.55\,\text{eV}$ [138, 139]. Qian and Chadi concur [150], as do Stekolnikov *et al.* [172], although this contradicts what is probably a typographic error in an earlier paper [15] where they mention the corner hole band pinning the Fermi level. Of all the calculations only Brommer *et al.* report significant LDOS over the corner hole atoms from $\sim-0.5\cdots+0.1\,\text{eV}$, suggesting that it is partially filled. None report a corner hole band as low as the restatom dangling bonds. Nevertheless the consensus is that the corner hole state is well below the Fermi level, and fully occupied.

**Adatom States**

The lowest lying surface state $S_3$, is at -1.8 eV and, based on ARPES polarization dependance [107], and STS imaging [64], is attributed to adatom backbonds, not one
of the dangling bond states.

The truly interesting $7 \times 7$ surface states are the ones associated with the adatom dangling bonds. These 12 subbands are loosely bunched near the Fermi level and are only partially filled. Measurements by ARPES, and KRPES have identified five bands: $S_1'$ at $-0.5 \text{ eV}$ is fully occupied and only resolvable at low temperatures, $S_1$ which has maximal intensity at $\sim -0.15 \text{ eV}$ disperses across and is believed to pin the Fermi level [40, 187], the lone unoccupied band $U_1$ is at $+0.55 \text{ eV}$ [131, 74, 134]. STM experiments have spatially identified these bands and linked them all to adatoms: $S_1$ and $U_1$ to corner adatoms in both HUCs, and $S_1'$ to corner adatoms predominantly in the FHUC [64, 125, 144]. More recent STS measurements have identified two new unoccupied bands $U_1'$ at $+0.20 \text{ eV}$ and $U_1''$ at $+0.41 \text{ eV}$ (they also place $U_1$ at $0.33 \text{ eV}$, substantially lower than the IPES result) [125]. The former has a mixed nature with intensity over both the corner and edge adatoms, the latter is mostly over the edge adatoms.

The various theoretical models universally agree that the 12 adatoms’ states are a tangle of subbands near the Fermi level that are individually weakly dispersive, but when taken together cover a wider energy range than the restatom manifold [28, 138, 139, 172, 150, 171]. The calculations also concur that the adatom states pin the Fermi level near midgap, but they predict different energy ranges. The inequivalency of the different types of adatoms is also a general feature: the lowest lying fully occupied state is associated with the faulted corner adatoms, but the states closest to the Fermi level are linked to both the corner and edge adatoms in both HUCs [139, 171, 27]. This is consistant with the sequence found by STS in Ref. [125].
Figure 3.7: STM Images of 7×7. a & b) Filled and empty state images. The faulted and unfaulted HUCs can be distinguished in the filled state image by their relative brightness. Within the faulted half the corner adatoms appear slightly brighter than the edge adatoms. The elongated UC shape is because of drift. In the empty state image the adatoms have uniform height. Image area \( \sim 10 \times 10 \text{nm}^2 \).

3.7 STM Imaging of 7×7

A pair of STM images by the author of 7×7, one of filled states the other of empty states, are shown in Figs. 3.7a&b. For both biases, the unit cell is easily visualized as the area demarcated by the dark corner holes. The empty state image on the right shows six clearly resolved adatoms in each HUC. The protrusions all have identical heights and diameters. On the other hand, for the filled state image on the left there is a distinct difference between the adatoms in the faulted and unfaulted half unit cell. The six adatoms in the faulted half appear brighter than their counterparts in the other HUC and the three faulted corner adatoms are brighter than the faulted edge adatoms. In the filled state image the restatoms are also visible and in this particular image, thanks to a cooperative tip, they are unusually well defined. In general, the interpretation of the features in STM images will follow this: bright protrusions in
.empty state images will be taken as adatoms. Protrusions that lie between adatoms in filled states, but are not visible in empty states, will be interpreted as restatoms. Finally, the brighter HUC in filled states will indicate the faulted HUC.

### 3.8 Other DAS Reconstructions

The 7×7 reconstruction is only one of many DAS reconstructions that have periodicity $N \times N$ with odd $N$, and share the DAS structural motifs. In particular, the 9×9 and 11×11 reconstructions have been observed for rapidly quenched Si(111) surfaces [18, 216]. However, of central importance for this study is the 5×5 reconstruction which is shown in Fig. 3.8. This reconstruction can be formed through rapid quenching of Si(111) from the high temperature 1×1 phase [216], by annealing of the cleaved Si(111)2×1 reconstruction [44, 45], or by depositing several bilayers (BL) of Ge onto Si(111). Only in the last case is 5×5 the lowest energy reconstruction; the others are metastable phases. This Ge overlayer 5×5 will be the one concentrated upon for this work. Here the focus will be on the reconstruction geometry. Details of its preparation will be left for Ch. 5.

The structure of 5×5 is shown in Fig. 3.8. The total number of atoms in the 5×5 DAS reconstruction is shown in Table 3.2. Two important structural differences between of 5×5 with 7×7 are that all adatoms are corner adatoms, and that there is only one restatom in each HUC. Table 3.2 also gives atom counts for a general $N \times N$ reconstruction. The total number of dangling bonds is reduced to 9, a density of 0.360/1×1, lower even than 7×7. Interestingly, there are exactly 50 atoms in the 5×5 selvedge layer, the same number as a bilayer of the ideal surface. So, uniquely among DAS reconstructions, 5×5 does not require a source or sink of atoms to populate the
3.9 Preparation of Si(111)7×7

A standard preparation routine was developed to generate clean, well-ordered surfaces to serve as substrates for all future growth. Wafer samples of 17 mm × 6 mm of p-type Si(111) with resistivity of 10-16 Ω cm were cleaned by boiling in ethanol, prior to UHV introduction. They were subsequently degassed at 800°C overnight. Once degassed a sample underwent repeated cleaning cycles that consisted of a 40 s flash where the temperature was ramped from 1250°C to 1100°C (heating current 10.0-12.0 ACA), followed by a quench to 850°C for 180 s to order the reconstruction, then a long ∼ 5 min anneal before beginning the next cycle. The cycles were repeated until the flash pressure remained < 1 × 10⁻⁹ Torr. This procedure reliably created very clean,
### Table 3.2: Atoms in the DAS reconstructions.

The table shows the number of each type of atom found in the 7×7, 5×5, and the general N×N reconstruction. For N×N, there are many different types of adatoms; the value given is the total.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Type</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>7×7  5×5  N×N</td>
</tr>
<tr>
<td>Adatom</td>
<td>Corner Adatoms</td>
<td>6  6  (\frac{1}{4}(N^2 - 1))</td>
</tr>
<tr>
<td></td>
<td>Edge Adatoms</td>
<td>6  0  (\frac{1}{4}(N^2 - 1))</td>
</tr>
<tr>
<td>Restlayer</td>
<td>Restatoms</td>
<td>6  2  (\frac{1}{4}(N - 3)(N - 1))</td>
</tr>
<tr>
<td></td>
<td>Interior</td>
<td>36 18  (\frac{3}{4}(N^2 - 1))</td>
</tr>
<tr>
<td>Dimer</td>
<td>Dimers</td>
<td>18 12 3(N - 1)</td>
</tr>
<tr>
<td></td>
<td>Interior</td>
<td>30 12 (N - 2)(N - 1)</td>
</tr>
<tr>
<td>Bulk 1</td>
<td>Top layer of bulk</td>
<td>48 24  N^2 - 1</td>
</tr>
<tr>
<td></td>
<td>Corner hole</td>
<td>1  1  1</td>
</tr>
<tr>
<td>Bulk 2</td>
<td>Bottom layer of bulk</td>
<td>49 25  N^2</td>
</tr>
</tbody>
</table>

**Figure 3.9: Examples of Prepared Si(111)7×7 Surfaces.** a) Large scale, 1 × 1 μm², image showing the step structure. b) Small scale, 50 × 50 nm², showing good cleanliness and surface order. V=2.0 V.
well-ordered Si(111)7×7, with large terraces and domains. Some examples are shown in Fig. 3.9.

3.10 Summary

This chapter introduced the DAS reconstruction. Its focus was on the 7×7 surface found on Si(111), but it also discussed the smaller 5×5 reconstruction that forms on Si(111)-Ge and will be of central importance to this work. The various components of the reconstruction were discussed, along with its symmetry properties and the electronic structure, in particular how that structure affects imaging with the STM. The chapter closed with a description of the preparation technique used here to clean and grow Si(111)7×7.
Chapter 4

Apparatus

This chapter briefly describes the microscope, UHV chamber, and sample preparation equipment used in this thesis. An accompanying chapter which provides details of the cooling stage is presented in Appx. A.

4.1 Overview

The experiments presented here were conducted in a custom manufactured ultra high vacuum (UHV) system. As shown in Fig. 4.1, it consists of two main chambers: the STM chamber houses the microscope and associated cooling and vibration isolation equipment while the preparation chamber contains the sample heating stage and evaporation sources. A fast entry loadlock is used to exchange samples and magnetic transporters (MDC MTM-24 and similar) move the sample holder around the system. The system is pumped with a turbopump (Varian Navigator backed by a Varian rotary), ion pump (Varian StarCell 300), titanium sublimation pump (Varian), and non-evaporable getter pump (SAES). At UHV only the latter three pumps are in use.
Figure 4.1: The STM System. Each side of the triangular support frame is 1.5 m.
and the base pressure is $< 7 \times 10^{-11}$ Torr.

Several design features ensure good vibration isolation. First, the microscope is situated in the building basement. Second, the entire system is suspended on pneumatic isolation legs (Newport). Finally, the sample and microscope head are isolated from the chambers by a stack of four massive rings damped by Viton spacers. On the top ring sits the “bloc massive”, a 5 kg mass that supports the sample stage. The use of fine 0.003” copper wires (California Fine Wires) for all electrical connections to the microscope minimizes the only other path for vibration transmission.

Aside from the microscope, the system is equipped with two diagnostic instruments. The first is a quartz crystal monitor housed in a custom holder. The holder was designed to have very low thermal mass. So, despite its lack of temperature control or monitoring it responds quickly to temperature changes (due, for instance, exposure to radiant heat flux from an evaporator). The second instrument is a mass spectrometer (MKS), useful for measuring residual gas content.

### 4.2 Microscope Head

The STM head is a beetle-type microscope [108, 112, 114]. It consists, as shown in Fig. 4.2, of three piezo legs arranged in a tripod surrounding a central scanning piezo tube. The legs are shod with ruby balls that walk on a polished metal table. Through repeated slip-stick cycles these three legs can walk the beetle in the $x$ and $y$ directions. The rectangular sample is mounted like a ramp at a 6° incline. Coarse approach is achieved by simply walking the beetle towards the ramp, until the tip comes into tunneling range. This design is known as a modified Wilms approach — modified, because the beetle legs straddle the sample asymmetrically rather than symmetrically.
in the original Wilms design [114, 204]. Its main advantage over the conventional Besocke approach is simplicity [53]: it requires simpler driving electronics, fewer control wires, and both the microscope, and in particular the surface upon which it walks, are easier to fabricate and polish. Once in tunneling range the central piezo tube is used to scan the surface, and the legs, through gentle bending, control the image location.

The tunneling current is measured by an air-side RHK IVP preamp with 100pA→1V gain. The microscope is controlled with an RHK SPM100 Controller and computer running SPM32 software.

### 4.2.1 Beetle Modifications

Several significant modifications were made to the beetle through the course of the work presented here. Most of the changes involve improvements to the scanner. In the original design, shown in Fig. 4.3a, the scanning tip was inserted into a PTCA
Socket (SPC Technology) which in turn fit into a stainless steel tube embedded into the scanning piezo tube. The skirt, a flared Al funnel connected to ground, shielded the tip from interference, particularly from the high rastering voltages applied to the scanner itself. A 0.003” Kapton coated wire (California Fine Wire) carried the tunneling current from the stainless tube up the piezo tube and to the top of the chimney. Aside from the Kapton insulation on the wire itself, ceramic tubes in the chimney and the scanner provided an additional layer of protection. Near the top of the chimney the fine wire was mated to a 0.010” Au coated Cu wire that protruded from the top of the chimney. A connector (AMP 50462-6) pushed onto this wire completed the circuit from the beetle to, eventually, the feedthrough and airside electronics.

After several years of use, it became apparent that there were several problems with the scanner design. First, PTCA sockets are not strictly UHV compatible, their sleeves are made from brass [170]. They also show a wide tolerance on the stem
CHAPTER 4. APPARATUS

diameter; so most PTCA sockets will not fit into the stainless tube. The stacking of a tip within a socket within a tube is redundant and invariably led to imprecise positioning of the tip height. Since, with a Wilms approach, the tip height directly affects where along the sample tunneling will be achieved, a badly positioned tip can be an unusable one. Also, the high currents (tens of mA) used for tip conditioning by aggressive field emission are enough to heat and degrade the fine wire carrying the tunneling current, leading to high impedance shorts between the tunneling wire and ground. This introduces noise in the tunneling signal and makes it impossible to apply high biases to the tip, necessary for procedures like tip annealing. Even without degraded insulation, the close proximity between the stainless tube and the grounded inner electrode of the piezo often led to short circuits when high biases were applied to the tip. Finally the 0.010” Cu wire used for the tunneling current connection was very flexible, which made the necessary connection difficult to engage and often unreliable.

To address these issues a new scanner design was adopted, and is shown in Fig. 4.3. A sapphire washer now sits at the end of the scanner, glued in place with non conductive epoxy. Into this is glued an AMP socket with its flare lying flush to the face of the washer. The socket is insulated from the interior electrode of the scanner with a \( \sim 5 \text{ mm} \) length of Kapton tube stripped from a UHV coax cable (MDC). The tunneling wire is now much thicker 30 AWG Kapton coated (MDC) and is bonded with conductive epoxy to the AMP socket at the bottom of the scanner, and to a 0.020” Mo pin at the top of the chimney. The connection to the Mo pin is made within a narrow alumina tube (Omega) which is fixed in the chimney with a set screw.

These changes solve the problems outlined above. The new AMP sockets are UHV
compatible and, since the tip inserts directly into the scanner, tolerance issues are eliminated and positioning precision improved. The heavier gauge wire permits high currents without risk to the insulation, and the large well-insulated gaps between grounded and high bias components eliminates arcing. Finally, the rigid pin at the top of the chimney makes connections simple and reliable.

Aside from the scanner changes, the beetle was upgraded with a new arrangement for making electrical connections for the nine channels which control the piezo movements. In the old scheme, PTCA sockets were pushed onto 0.010” Cu wire; the same method used for the tunneling wire and suffering from the same problems. The solution is identical: rigid 0.020” Mo pins glued into alumina tubes and fixed into the beetle chassis. Connections are made with AMP sockets (AMP 50462-6) and are more rigid, secure, and reliable than the old flexible wire connections.

### 4.3 Sample Holder

The sample holder is the vehicle which carries the sample within the chamber. It allows a small and fragile sample wafer to be moved from the load-lock for introduction, to the heating stage for cleaning, and then to the sample stage for scanning. It consists, as shown in Fig. 4.4, of three main parts: the body, the upper block and the lower block. The rectangular sample is secured to the blocks at either end under spring clips. The blocks hold the sample at the angle required for the approach and are themselves fixed to the body. The grooves in the body perimeter accept the transfer forks which are used to move the holder around the chamber. The upper block is electrically isolated from the body by ceramic washers. In contrast, the lower block is in direct electrical contact with the body. The sample is heated by passing a
current from one end of the wafer to the other. An electrical contact on the heating stage injects current into the upper block, which passes through the sample into the lower block, through the body and returns to ground through the fork supporting the sample holder. The construction materials are chosen for UHV compatibility, resistance to high temperatures, inertness towards high temperature Si, and immunity to cold welding. The blocks and clips are Ta, ceramics are alumina, and body and fasteners Mo.

The basic sample holder design is due to Jenny MacLeod [112] but the newest iterations include several important modifications. First, the tables on which the beetle walked were once part of the sample holder itself. With the advent of the cold stage, described below, these became part of the sample stage and were removed from the holder. This reduced outgassing during flashes, improved visibility during transfers, and eliminated Si and evaporant buildup on the tables. More subtly, the blocks were redesigned to reduce their thermal mass, thermal contact with the sample, and
improve the robustness of the ceramic isolators. Two new schemes were developed to make electrical connections to the upper block. In the first, a small contact protrudes from the bottom of the body and touches a complementary contact on the heating stage. In the second, the electrical contact is made through the very screws which fasten the block to the body. In the end both schemes have proven very reliable and are in use in two different STM systems. These incremental changes to the sample holder and heating stage have improved the reliability of the system considerably.

4.4 Tungsten Tips

In the past, almost all experiments conducted in this group were done with PtIr tips. These are easy to fabricate; stable, particularly in air; and recoverable in the event of a tip-sample collision. Despite these qualities, the majority of STM experiments reported in the literature use, not PtIr, but W tips. Our group had some experience with W tips, but had largely abandoned them in favour of simpler PtIr ones. The W tip program was resurrected by refurbishing the tip etching apparatus, commissioning new etching control hardware, and developing in-situ conditioning techniques.

In brief, sharp tungsten tips are fabricated by electrochemical etching in a basic solution. Our technique, adapted from Ref. [109] and references therein, immerses a short length of W stock wire and applies a constant positive bias versus a counterelectrode. The etching products form a viscous sheath that slides down the wire which partially protects the immersed section of wire. Etching, therefore, occurs preferentially where the tip meets the solution’s surface, and with time the wire necks there. Eventually the neck grows too narrow to support the immersed wire and it breaks leaving a sharp point: the tip. If etching continues the tip will be dulled, so control
electronics are used to switch off the etching current immediately upon drop off.

The heart of the apparatus is an old microscope frame, as shown in Fig. 4.5. The microscope stage supports the solution and the tip is held where the microscope’s objective lens once was. The frame is secure and rigid and the focus controls allow precise positioning of the tip depth. A custom built tip etching controller applies a DC voltage and monitors the etching current. When the current falls below a threshold, indicating drop off, the voltage is removed. Comprehensive testing by Brandon Ward found that optimal results are obtained with an etching solution of 9 molar KOH, an applied voltage of 9 V, and a threshold current of 10 mA. For standard 0.020” W wire, etching takes around 10 min. Etched tips are examined under an optical microscope and are considered acceptable if they show no rounding visible under
an optical microscope. The tip etching apparatus has proven easy to use, quick, and generates high yields; over 75% of the tips pass the (admittedly crude) quality control test.

To complement the new ex-situ tip preparation several new in-situ conditioning techniques have been developed. The first is tip annealing. Out of vacuum, W quickly develops an oxide layer that should be removed before scanning. At high temperatures WO$_3$ converts to WO$_2$ which sublimes leaving a clean W surface [35]. With no tip transfer available, our system of annealing heats the tip using electron bombardment while it is installed in the microscope. Heating for 2 s at 2000 V and 10 mA is enough to flash the tip apex without damaging the scanner that holds it. The second in-situ technique is self-sputtering. In this case the field emission between the tip and a metal surface ionizes a deliberately introduced Ne backfill. The positive Ne$^+$ ions are attracted to the negatively charged tip and sputter its surface removing contamination, and sharpen the apex.

In practice, neither annealing nor sputtering proved necessary on a regular basis. The tried and true repertoire of field emission, high current tunneling, and controlled crashes was sufficient for conditioning tips, even for newly introduced, and presumably oxide coated, W tips.

4.5 Thermometry

Sample preparation requires a complex series of heating and cooling steps performed according to a defined recipe. Some steps are robust against variations in sample temperature (e.g. sample flashing), but others (e.g. annealing Ge overlayers) are sensitive. Three different techniques are discussed here for measuring the sample
temperature based on thermocouples, pyrometry, and current. It will be seen that they all suffer some deficiencies, but that taken in combination a useful temperature measurement scheme can be assembled.

Thermocouples and pyrometry are widely used and well characterized techniques. In brief, a thermocouple is a junction of dissimilar metals which generates a voltage that is related to its temperature. The junction can be used to measure the temperature of an object with which it has been placed into direct thermal contact. A pyrometer measures the radiation emitted by an object and, by knowing Planck’s Law and correcting for its emissivity, measures its temperature without direct physical contact.

Unfortunately, both techniques suffer deficiencies which limit their usefulness in this application. Responsive measurements and low thermal load requires a fine gauge thermocouple which, with prolonged exposure, melts at temperatures lower than those required to clean Si. Also the sample holder and heating stage are simply not equipped to make measurements from a thermocouple and allow sample movement about the chamber. Finally, and most seriously, the most widely used thermocouples all contain nickel, a powerful surface catalyst. Nickel, when placed into direct contact with a Si wafer, makes preparing ordered reconstructions impossible – Ni contamination is such a concern that Si wafers are never handled with stainless steel tools.

A pyrometer, since it measures remotely, cannot contaminate the sample. But at low temperatures Si is IR transparent. This low temperature regime is important for the preparation of adsorbate covered systems. Also, since a pyrometer sights the sample through one of the UHV windows its accuracy is diminished by the buildup that comes with repeated cleaning and evaporation cycles.
The third thermometry technique measures the current passed through the sample. In the simplest approximation at steady state the power input $P$ will be balanced by the heat lost to radiation and conduction. So the temperature of the sample is a function only of the power being applied to it, $T(P)$. Since the sample is heated by passing a current $I$ through it, the power is simply $P = IV = I^2R(T)$. The resistance of Si is a function of its temperature: at low temperatures conduction is dopant dominated, and its temperature behaviour is complicated. At higher temperatures thermally promoted carriers dominate and the resistance follows a simple form related to the Fermi distribution [41]. In either regime, the temperature of the sample will be determined by the current passing through it $T(I) = T(I^2R(T))$. In practice, this is taken as true and the sample temperature is effectively measured in Amps. But what are the limits to the validity of this approximation, and what is the conversion factor between current and true temperature?

To investigate these questions, a special sample heating stage was fabricated specifically for testing. The sample was a 17 mm × 6 mm wafer of $p$-type Si(111) with resistivity of 10-16 $\Omega$ cm. Simultaneous measurements were made of the sample current and voltage, along with temperature measurements by pyrometer (Land System4 Type M1) and thermocouple. The K-type thermocouple was made by spot welding two 0.003” wires together and pressing the resulting junction against the surface of the sample. Once in vacuum, momentarily raising the sample temperature to $\sim$1100° C melted the junction into the surface, forming an ideal thermal link. Without the embedding step the thermocouple consistently read $\sim$300° C lower than the pyrometer. The fine thermocouple wires led to extremely low conductive heat losses, but could not withstand prolonged exposure to high temperatures. Since the sample was
never intended for surface studies there was no concern about contamination.

Figure 4.6 shows the behaviour of sample temperature with current. Below \( \sim 350^\circ \) C the pyrometer stops measuring, but it gives reasonable results even below 600\(^\circ\) C, its lowest rated temperature. Between 600\(^\circ\) C and 900\(^\circ\) C the largest deviation between the thermocouple and pyrometer reading is 8\(^\circ\) C. Figure 4.7 shows how the resistance of the Si sample changes with temperature. At high temperatures (plot left) the relationship is linear indicating intrinsic behavior. The slope corresponds to \( E_g/2k \) where \( E_g \) is the Si bandgap energy at 0K. [41]. Several such measurements from similar samples yield band gap of a 1.14\( \pm \)0.02 eV for thermocouple measurements and 1.25 \( \pm \) 0.02 eV for pyrometer measurements. These are in good agreement with published values of 1.17 to 1.205 eV [41].

At low temperatures (the inset to Fig. 4.6 and to the right of Fig. 4.7) the
resistance is dopant dominated and non-linear. Pyrometry does not work at these temperatures, and for samples intended for study thermocouples are out of the question. Thus, for low temperature preparations, the calibration curve of Fig. 4.6 will be used to measure the sample’s temperature based on the current passed through it.

### 4.6 Evaporators

A basic requirement of this project was the ability to apply to a clean surface high-purity adorbates at small, often sub-monolayer, quantities and specific rates. Home-built evaporator sources were used to do this. The principle of operation for an evaporator is simple: as the temperature of an evaporant is raised so too does its vapour pressure. Since the chamber pressure regime is molecular flow the vapourized atoms of evaporant travel ballistically outwards from the source; if the sample
Figure 4.8: Evaporators. a) Mg crucible evaporator. b) Ga basket evaporator.

is placed with line of sight to the source it will be covered with a film of evaporant whose thickness depends on the time of exposure, and distance to and temperature of the source. Although the theory of evaporator operation is simple, the practice tends to be fraught with complication.

4.6.1 Magnesium

The Mg evaporator, shown in Fig. 4.8a, consists of a quartz crucible (Lesker) wrapped with a homemade 0.010” Ta filament. A prism of Mg cut from 1 mm thick sheet lies within the crucible. The vapour pressure of Mg is very high and it sublimes from solid at low temperature. Operation at 1.7 A gives 0.5 Å/min.

4.6.2 Gallium

The Ga evaporator is a basket style source as shown in Fig. 4.8b. A 0.007” W wire, formed on a conical mandrel, supports a small droplet (~3mm diameter) of 9N
CHAPTER 4. APPARATUS

Gallium. A Ta foil shroud (not shown) shields the assembly. Operating at 2.7 A gives \( \sim 0.3 \text{ Å/min} \).

4.6.3 Indium

This evaporator uses a custom quartz crucible \( \sim 10 \text{ mm} \) in diameter wrapped with 0.015" W wire. Operating at 2.7 A gives 0.04 Å/min. The large crucible volume and low required rates (and consequently low operating powers) made this a very long lived evaporator.

4.6.4 Aluminum

The aluminum evaporator follows the design of [210]. It uses a 0.0625" diameter alumina tube as an ersatz crucible. The tube is wound with a coil of 0.007" W wire. Thin strips of 5N Al foil were inserted into the tube. Operation at 2.4 A gives \( \sim 0.12 \text{ Å/min} \), but this evaporator never produced reliable rates.

4.6.5 Germanium

Several different Ge evaporator designs were attempted involving large alumina crucible evaporators, smaller BN crucibles, tiny basket evaporators, and electron bombardment heated Mo and Ta crucibles. All suffered from excessive power consumption leading to poor cleanliness and/or unreliability. The problems largely stemmed from the demands imposed by the high temperatures required for Ge evaporation, and the chemical reactivity of Ge at those temperatures, coupled with the desire for thick coverages (a requirement that was later relaxed). The final design, shown in Fig. 4.9, used for all the results presented here, is an unorthodox combination of a basket for
support with heating provided by electron bombardment. A Ge bead (Lesker, 5N purity) is supported in a 0.012” W basket and heated by electron bombardment from the 0.005” W filament. This is assembled as a cartridge that can be exchanged into a water cooled stainless steel shroud, designed by Jay Weymouth. During operation a constant +1700V bias is applied to the basket and the filament current is varied under the control of software to maintain a constant power delivered to the evaporant. The direct heating of the evaporant, without intervening crucible means that very low powers are required; 3-4W is sufficient to produce $\sim 1 \text{Å/min}$ with pressures $< 2 \times 10^{-10}$ Torr. One interesting and unexplained quirk in its operation is that a short burst of high power is necessary to start evaporation, whereupon the power can be reduced to the normal operating levels. Roughly 7-10W for 2 min is necessary to kickstart evaporation, before the power can be throttled back.
Chapter 5

Germanium Growth

Part of the beauty, and utility, of surface growth is the wide variety of structures that can be formed by the growth of adsorbates. Control over the structures comes from the choice of adsorbate, its rate of delivery, and the temperature and sequence of the operations performed. This chapter attempts to summarize the principles that govern the growth of those structures. It deals explicitly with two different length scales: the *atomistic*, how individual atoms behave; and the *mesoscopic* the collective behaviour of the thin film. These principles will be applied to the growth most important for this work: epitaxy of Ge on Si(111). Of course, the full richness of growth at surfaces cannot be summarized in a single chapter. More complete treatments can be found in the books by Venables [189], Zangwill [222] and Barabási [9]. Like Ch. 3, most of the material presented here is received knowledge in the field, presented in the author’s style. However, the final section deals with specific preparation routines developed and used by the author.
CHAPTER 5. GERMANIUM GROWTH

5.1 The Atomistic Scale

Of course different adsorbates deposited on different substrates will form different structures. Growth in the technique of molecular beam epitaxy (MBE) is determined by several different processes illustrated in Fig. 5.1: adsorption, desorption, diffusion, intermixing, nucleation and growth.

The lifecycle of an adsorbate atom on a surface has several different stages and possible outcomes. The first step is the arrival and attachment of the adsorbate atom to the surface. This is an exothermic process and the energy given off is the adsorption energy $E_a$. Conversely, this energy represents the barrier faced by the adatom to re-evaporation. When the temperature is high enough that the thermal energy is comparable to this barrier, the adatom may desorb from the surface and be lost to the vacuum.

Once on the surface, the adatom faces a barrier to movement to adjacent sites of $E_d$. If the thermal energy is high enough to overcome that barrier, then the adatom will diffuse, moving from local minimum to minimum on the potential energy surface.
CHAPTER 5. GERMANIUM GROWTH

Certain sites on the surface like steps, vacancies, impurities, and domain boundaries, are distinct from the other identical sites that make up the rest of the surface. These special sites may have a higher binding energy, and if the adatom lands on or diffuses to one the higher affinity will cause it to stick there, even if the temperature is high enough to allow diffusion between normal sites. Alternatively, if in its travels a diffusing adatom meets another diffusing adatom the two can bind together with energy $E_b$ and, generally, will become rooted to the surface. This process, nucleation, is non-linear: it requires two mobile adatoms to arrive in coincidence. Again, if the temperature is high, the binding energy can be overcome and the nucleus will break up; a type of 2D evaporation. If more adatoms attach to the nucleus before it disintegrates they will strengthen its cohesion and resist breakup. As the island’s area grows it becomes more stable since atoms can only leave from its perimeter and the interior atoms are geometrically confined. Above a critical number of atoms $i^*$ the cluster will be stable in the sense that it captures more atoms then it loses: the cluster will grow. Clusters containing $i^*$ or fewer atoms will eventually disintegrate.

The final important process is intermixing, where an adsorbate atom exchanges with a substrate atom. This is 3D diffusion and, in general, there is a higher barrier to this process than for 2D diffusion. Intermixing can be driven by entropy or enthalpy, in Ge islands we will see a case of strain mediated intermixing.

We now turn to examining the formation of clusters and islands on a surface, through these growth processes. To make things simpler we assume a singular surface, one with no steps, defects or other special sites, and temperatures low enough to suppress intermixing. If the barrier to desorption is $E_a$ then the lifetime of a free
CHAPTER 5. GERMANIUM GROWTH

Figure 5.2: Island Growth. A cluster of any size can exchange atoms with the bath of mobile adatoms. Gaining an atom moves the island size to the right ($j \to j + 1$) and decreases the number of mobile adatoms by one. Losing an adatom does the opposite. At and below the critical size $i^*$, the number of adatoms lost and gained are, on average, balanced. Above the critical size, the increased binding energy makes clusters stable against decay, so on average the flow is into growth rather than decay.

adatom before desorption is

$$\tau_a = \nu^{-1} \exp\left(\frac{E_a}{kT}\right), \quad (5.1)$$

where $\nu$ is the attempt frequency. The diffusion rate is given by

$$D \sim \nu \exp\left(-\frac{E_d}{kT}\right). \quad (5.2)$$

All adsorbed adatoms will either have desorbed, or be found as either individual adatoms, nucleated pairs, or larger clusters. The densities of such formations are denoted as $n_1$, $n_2$, or $n_j$ for $j$-sized clusters, see Fig. 5.2. The number of adatoms
freely diffusing is governed by

\[
\frac{dn_1}{dt} = F - \frac{n_1}{\tau_a} - 2U_1 - \Sigma U_j.
\] (5.3)

The terms are described pictorially in Fig. 5.2. The first term on the right \( F \) is the flux of arriving adatoms. The remaining terms account for the fate of those adatoms; the second describes the evaporation of adatoms, \( \tau_a \) is the time constant for re-evaporation. \( U_j \) is the net capture rate of adatoms by \( j \)-sized clusters, so \( 2U_1 \) accounts for nucleation and the sum tallies growth. Clusters of \( j \geq 2 \) grow through the addition of single adatoms to an existing cluster, so the number of such clusters is governed by

\[
\frac{n_j}{dt} = U_{j-1} - U_j.
\] (5.4)

We can collect together all of the stable clusters for which \( j > i^* \) and refer to their number as \( n_x \). As Fig. 5.2 shows, all clusters of size \( j > i^* \) must grow, originally, from clusters of size \( i^* \) the rate equation for these stable clusters is

\[
\frac{dn_x}{dt} = \sum_{j>i^*} (U_j - U_{j+1}) = U_{i^*}. \] (5.5)

These can be combined to yield

\[
\frac{dn_1}{dt} = F - \frac{n_1}{\tau_a} - w_x \frac{dn_x}{dt} \] (5.6)

\[
\frac{dn_j}{dt} = 0 \quad (2 \leq j \leq i) \] (5.7)

\[
\frac{dn_x}{dt} = U_{i^*} \sim Dn_1 n_{i^*}. \] (5.8)
The last term of the first equation expresses the depletion of the reservoir of free adatoms in terms of the number of stable islands and the average size $w_x$ of those islands. For unstable clusters, $2 \leq j \leq i^*$, the increase in the number of islands that comes from adatom capture by $j-1$ sized islands or decay by $j+1$ sized islands is balanced by the $j$-sized islands that themselves lose or capture adatoms. So the net change in number for all clusters below the critical size is zero. Finally, the last equation writes the net increase in number of stable islands in terms of the diffusion rate $D$, the number of free adatoms, and the number of critical islands. Additional terms can be added to the last equation to account for merging of clusters and direct impingement of arriving flux.

In the limit of no re-evaporation, known as complete condensation, $\tau_a \gg 1$ the density of stable clusters is given by [190]

$$n_x \sim \left( \frac{F}{D} \right)^{\frac{i^*}{i^* + 2}} \exp \left( \frac{E_{i^*}}{(i^* + 2)kT} \right)$$

(5.9)

where $E_{i^*}$ is the binding energy of the critical cluster. This expression highlights a general theme in surface growth (and many other fields): the final outcome is a the balance between kinetics ($F$), and thermodynamics ($D$) [12]. In the kinetic regime ($F/D \gg 1$) many small islands form. In the thermodynamic regime ($F/D \ll 1$) fewer, but larger, islands grow. The intermediate domain between these two extremes allows interplay between kinetics and thermodynamics. It’s possible to think of the system as finding a local thermodynamic minimum. The length scale (i.e. how local is local) is ruled by the kinetics. Once the choice of surface and adsorbate is made, the parameters left to the experimenter’s control are adsorbate flux ($F$) and the temperature ($T, D(T)$). These are the two macroscopic control knobs available to
tune the growth of the overlayer.

5.1.1 The Effect of the Reconstruction

The simple picture presented above is complicated if the surface has a reconstruction. A reconstructed surface affects the growth process in two respects. First it makes more intricate the potential energy surface for diffusing adatoms. In the case of DAS reconstructions, for example, diffusion within the HUC is relatively easy, but diffusion from one HUC to another is impeded by the dimer wall that separates them. Secondly, reconstructions lower the total energy by rearranging the surface atoms. For epitaxial growth the reconstruction must revert to its bulk position — it must “de-reconstruct”. This is a kinetic barrier. In particular, for DAS, the stacking fault and the dimer rows that surround the HUCs are stable structures that must be “de-reconstructed” before further growth can proceed.

5.2 The Mesoscopic Scale

Having discussed the behavior of atoms on the surface, it is productive to view the growth process on the length scale of nanometers. This is a scale larger than that of individual atoms, so that they can be thought of as a collective and continuum techniques applied [68]. This perspective is particularly helpful when dealing with thicker coverages in the thermodynamic regime (D/F ≫ 1) where a discussion of energy minimization is meaningful.
5.2.1 Growth Modes

In this picture there are three surface energies of interest. The surface energy of the interface between the substrate-vacuum $\gamma_s$, the adsorbate-vacuum $\gamma_a$ and the substrate-adsorbate $\gamma_i$. The goal of the system is to minimize the total surface energy, and in the thermodynamic regime it will do just that.

There are two obvious ways that a surface can grow. The first is layer-by-layer; the adsorbate wets the surface. The second is by the formation of three dimensional islands; the adsorbate balls up on the surface. The energy per unit area for the former case is $E_1 = \gamma_i + \gamma_a$. The energy of the latter (assuming, for the sake of argument $\frac{1}{2}$ area coverage, and thin 3D islands) is $E_2 = \frac{1}{2}(\gamma_i + \gamma_a + \gamma_s)$. The energy difference between the two possibilities is $\Delta E = \frac{1}{2} \Delta \gamma$ where

$$\Delta \gamma = \gamma_i + \gamma_a - \gamma_s. \tag{5.10}$$

If $\Delta \gamma > 0$ then the adsorbate will ball up. This is called Volmer-Weber growth. If $\Delta \gamma < 0$ the adsorbate will grow layer-by-layer, known as Frank-Van der Merwe growth. But beyond these obvious mechanisms a third mode is possible: growth that begins layer-by-layer can transition to island growth if the interfacial energy between
one layer of adsorbate and the next increases with thickness. This third growth type, 3D islands upon a wetting layer, is known as Stranski-Krastanov growth. The mechanism that causes the increase in $\gamma_i$ is often intermixing or strain.

5.2.2 The Effect of Strain

If two materials have the same crystal structure, but different lattice constants, when one is deposited upon the other the growth behavior will be affected by the mismatch in lattice constant. If the smaller lattice material is deposited on the larger lattice one the result will be tensile strain in the overlayer, the opposite arrangement leads to compressive strain. The responses to this strain are determined by the magnitude of the lattice mismatch and the strength of the bonding between the adsorbate and substrate [95, 122]. In cases where the adsorbate bonding is weak, the adsorbate grows layer-by-layer but out of registry with the substrate. It simply grows according to its own bulk lattice spacing and ignores the substrate beneath it. This is known as floating mode growth.

Growth in the pseudomorphic mode occurs when the adsorbate-substrate binding is strong, and the lattice misfit is small. In this mode, growth proceeds layer-by-layer and the overlayer is strained. The buildup of strain energy with increasing thickness in the overlayer means that such growth cannot proceed indefinitely. To relieve the strain in thick layers the growth transitions from layer-by-layer to island type. So adsorbates which grow in the pseudomorphic mode inevitably exhibit SK growth and pseudomorphic islands grow. The islands' walls are unconstrained (unlike the wetting layer), so they can relieve strain by simply relaxing laterally from one layer to the next. The substrate, by locally buckling under the island, can also help to relieve
Figure 5.4: Strained Growth Modes. A lattice mismatch between the substrate and adsorbate leads to different growth modes. Adapted from [68]
the strain [95]. All of this is done by distorting the crystal, but without introducing crystal defects. Just as there is an upper limit to the thickness of a pseudomorphic wetting layer, there is a maximum size of pseudomorphic islands defined by the ratio of strain energy throughout the island interior and the degree it can be relieved by distortion at its walls and top.

Strain can also be relieved through the introduction of defects. In the dislocation mode the overlayer is largely registered to the substrate, but dislocations between the two serve to periodically relieve the strain. The energy of the system is a balance between the cost of introducing dislocations, the strain, which the dislocations reduce, and the surface energies. Roughly speaking, a dislocation relieves strain in any number of layers above it. So the most efficient way to relieve strain is to stack many layers upon a small number of dislocations, leading to island growth. Since the gain from dislocations comes at the expense of creating the dislocations in the first place, the minimum energy system may not be one with higher strain, but fewer more efficiently organized dislocations [164].

Intermixing does not relieve strain so much as distribute it. By exchanging adatom between the substrate and the overlayer the strain energy is dispersed over a larger volume. This is a case of strain mediated diffusion. In a related mechanism strain can encourage the formation of a trench at the base of an island where the strain is highest [8]. Material flows up and out of the trench and distributes either on the island itself or the surrounding terrace. This leads to strain relief through relaxation of the island edge. In reality these four mechanisms will work in concert when overlayer strain is important.
### Table 5.1: Legend for Si(111)-Ge Phase Diagram, Fig. 5.5

Each row describes a different phase, first identified in Ref., and corresponding to the temperature-coverage coordinate indicated by ID in Fig. 5.5. Figures a, f, g, i, k, and l are reprinted with permission from the American Physical Society. Figures b–e and j are reprinted from with permission from Elsevier. Figure h reprinted under Creative Commons license.

<table>
<thead>
<tr>
<th>ID</th>
<th>Description</th>
<th>Coverage (ML)</th>
<th>Temp. (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Bonding at $B_2$ sites</td>
<td>∼0.01</td>
<td>21</td>
<td>[228]</td>
</tr>
<tr>
<td>b</td>
<td>Clusters</td>
<td>0.1</td>
<td>∼21</td>
<td>[4]</td>
</tr>
<tr>
<td>c</td>
<td>Dense Clusters</td>
<td>0.3</td>
<td>∼21</td>
<td>[4]</td>
</tr>
<tr>
<td>d</td>
<td>Cluster Array</td>
<td>0.5</td>
<td>∼21</td>
<td>[4]</td>
</tr>
<tr>
<td>e</td>
<td>Growth over Clusters</td>
<td>0.7</td>
<td>∼21</td>
<td>[4]</td>
</tr>
<tr>
<td>f</td>
<td>Amorphous Overlayer</td>
<td>4</td>
<td>∼21</td>
<td>[72]</td>
</tr>
<tr>
<td>g</td>
<td>Si Adatom Substitution</td>
<td>0.02</td>
<td>150</td>
<td>[197]</td>
</tr>
<tr>
<td>h</td>
<td>g + Clusters</td>
<td>0.12</td>
<td>∼100</td>
<td>[198]</td>
</tr>
<tr>
<td>i</td>
<td>g + Cluster Array</td>
<td>0.5</td>
<td>150</td>
<td>[111]</td>
</tr>
<tr>
<td>j</td>
<td>g + 2D Islands of $5\times5$ and $7\times7$</td>
<td>1.35</td>
<td>500</td>
<td>[124]</td>
</tr>
<tr>
<td>k</td>
<td>5×5 Wetting Layer</td>
<td>∼3</td>
<td>∼500</td>
<td>[116]</td>
</tr>
<tr>
<td>l</td>
<td>k + 3D Islands</td>
<td>6</td>
<td>400</td>
<td>[143]</td>
</tr>
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</table>

### 5.3 Germanium on Si(111)

Like Si, bulk Ge has the diamond crystal structure. However, Ge’s lattice constant is bigger than Si’s by ∼4% (5.66 Å for Ge vs. 5.43 Å for Si). The strain that results allows the band gap of mixed Ge-Si alloys to be engineered, but it also leads to interesting growth phenomenon at surfaces. The phase diagram for MBE growth of Ge on Si(111), shown in Fig. 5.5, demonstrates the richness of possible growth outcomes with only two control parameters: Ge coverage and substrate temperature. The system is comparatively insensitive to the effect of deposition rate and deposition sequence, but these do have important effects and will be discussed later.

There are four kinetic processes which largely determine the behaviour of Ge adsorbates on the $7\times7$ surface. The lowest energy process is Ge substitution for Si adatoms. The second is diffusion of adatoms between HUCs. The third is dissolution
Figure 5.5: Phase Diagram of Ge on Si(111)7×7. Refer to Table 5.1 for legend.
of clusters, and finally the lifting of the stacking fault in the DAS reconstruction. The phase diagram can be roughly divided into three temperature ranges which correspond to these processes: low temperatures (<100°C) where behaviour is close to hit and stick, moderate temperatures where substitution and short range diffusion take place, and high temperatures (>350°C) where long range diffusion becomes possible.

5.3.1 Low Temperature Regime

At temperatures below \( \sim 100^\circ\text{C} \) the behaviour of Ge is close to hit and stick. There is insufficient energy to disrupt the \( 7 \times 7 \) reconstruction, but the effective bond saturation of the reconstruction means that bonding at many areas of the surface is energetically untenable. Specifically, the dimer rows which surround each HUC are entirely saturated, so they are unfavorable bonding sites and strong barriers to diffusion. Thus the adsorbed Ge adatom is essentially restricted to the HUC in which it landed [211].

Low Coverages - Basins of Attractions

At low coverages (\( \lesssim 0.05\text{ML} \), region \( B2 \) in Fig. 5.5) deposited Ge bonds at two distinct but related sites, \( B_2 \) near the corner adatom, and \( B'_2 \) near the edge adatoms (there is some suggestion the optimal bonding site is displaced slightly from the high symmetry points [228]) [5]. Adsorption at \( B_2 \) is stable and in STM images the Ge adatom shows up as a protrusion displaced slightly from a corner adatom. However, adsorption at the \( B'_2 \) site, which calculations show is slightly preferred energetically, is unstable: there are six equivalent \( B'_2 \) sites in close proximity to one another and, since the energy barriers between them are low, the Ge adatom hops rapidly between them.
The result is a blurry protrusion in room temperature STM images as the adatom diffuses around the basin of attraction at the centre of the HUC [228]. Neither of these states is a global thermodynamic minimum, but the kinetic barrier cannot be overcome without higher substrate temperatures.

A coverage of 0.12 ML corresponds to an average of 3 Ge adatoms in each HUC. The multiple adatoms in each unit cell start to form clusters (region Cl in Fig. 5.5) [225, 213, 212, 61, 4, 152]. Since the temperature is low, the clusters are not annealed and their appearance is irregular, but the dimer rows continue to restrict clusters to forming in the interior of the HUC. At higher coverages more clusters form, up to \( \sim 0.5 \) ML (12 atoms/HUC). At this point there are large clusters in every HUC, and the surface takes on a honeycomb appearance called a cluster array (region Cl Array in Fig. 5.5).

Further coverage leads to patches of second layer growth on top of the cluster array [213, 4]. There is no discernable regularity to the overgrowth. This amorphous layer grows more complete and thickens with increasing coverage (region \( a \)-Ge on Fig. 5.5). Interestingly, for low temperature deposition diffraction techniques, which can probe the Si-Ge interface and for which the \( a \)-Ge layer is largely invisible, show that the Si surface retains a so called \( \delta-7\times7 \) pattern [56, 72, 73]. This indicates that the \( 7\times7 \) adatom periodicity is lost, but the stacking fault and dimers remain intact. Effectively, for low temperature deposition the \( 7\times7 \) reconstruction is buried.

### 5.3.2 Moderate Temperatures

Above \( \sim 100^\circ \text{C} \), but below \( \sim 350^\circ \text{C} \) the adsorbate Ge atoms have enough energy to engage in inter-HUC diffusion and adatom substitution.
At low coverages ($\lesssim 0.12$ ML) the $7 \times 7$ reconstruction remains intact and Ge substitutes for Si adatoms. This was first suggested by XSW measurements [142], later was supported by REM/TED [89] and core-level photoemission [30], and finally confirmed with STM [197, 228, 5, 198] and AFM [217] backed up by calculations [197]. In filled state STM images the Ge adatoms appear slightly higher than the native Si ones, but not as high as Ge atop Si. The images show no sign of asymmetry in the shape of a Ge adatom, an indication that the displaced Si adatom has departed.

Close examination after incremental Ge exposures shows that substitution is almost uniform at the lowest coverages (0.02 ML), but at higher coverages (>0.08 ML) a large majority of substitutions (>65% [197]) occur for the corner adatoms in the FHUC. Calculations indicate that the configuration with adatoms at the nearby $B_2$ sites is essentially energy degenerate. In practice the displaced adatoms are never observed here, but calculations show that atoms at these sites are mobile (which, as shown above, was reaffirmed by Ref. [228]). At elevated temperatures, these adatoms can migrate and attach to nearby step edges or nucleate islands. These islands are indeed observed [197]. Thus, the displaced adatoms coalesce leaving behind mixed species, but undecorated, $7 \times 7$.

Like the cooler substrate, at higher coverages the extra Ge adatoms begin to coalesce into clusters. Because of the higher mobility, clusters formed at moderate substrate temperatures are more uniform, and demonstrate a higher preference for FHUC formation than those grown at room temperature [61]. Measurements suggest a critical cluster size of $7.5 \pm 1$ Ge atoms, roughly the same as for Si [6]. A variety of different cluster shapes have been observed which correspond to distinct numbers and configurations of Ge atoms. The preferred cluster size is estimated to be 8 atoms,
not much larger than the critical size [111]. Filled state images of clusters in the
FHUC show charge depletion in the adjoining UHUCs. This has been substantiated
by calculations, which show that for all energy-minimizing configurations of clusters
between 6-12 Ge atoms, charge is transferred from adjacent UHUC edge adatoms to
the FHUC cluster. This makes the adjacent UHUCs preferred sites for further cluster
growth, an arrangement which locally reverses the normal FHUC preference and a
leads to the favouring of cluster pairs [111, 49]. At higher coverages this leads to a
percolation network of clusters that, at high coverages, becomes fully-covered.

5.3.3 High Temperatures

At high temperatures Ge adatoms have high mobility, clusters are unstable against
dissolution, and there is sufficient energy to cause the stacking fault, and surrounding
dimers, to revert to the bulk arrangement allowing pseudomorphic growth. In this
regime, the adsorbate behaves closest to the manner described in classical growth
theory; adatoms diffuse relatively freely, and attach at special sites or coalesce into
spontaneously nucleated islands all growing epitaxially on the surface. Larger scale
growth is governed by the interplay between strain, surface energy, and the cost to
initiate dislocations.

At the lowest coverages, the Ge adatoms continue to substitute for Si adatoms in
the $7\times7$ reconstruction, just as they do at lower temperatures [228]. As the coverage
increases, 2D epitaxial islands start to form with well-ordered reconstructions on their
top faces. At low coverages (0.04 BL) and temperatures at the low end of the range
small islands (2-6HUC) grow with uniform size, and high density [119, 176, 175]. At
higher coverages or temperatures the islands become triangular with the exposed faces
pointing along $<211>$ directions, which means the island is surrounded by FHUCs [119]. The substrate between 2D islands is $7\times 7$ with Ge adatom substitution. In many cases, at lower temperatures, clusters can coexist with the islands. In Si homoepitaxy similar islands are initiated by coincidence of several HUC clusters [49, 50]; a similar mechanism is likely at work with Ge.

The reconstruction exposed at the island surface is affected by the growth rate. At high growth rates (high $F/D$), when kinetically limited, many islands are $7\times 7$ but at lower rates the islands assume the dominant reconstruction $5\times 5$ due to the compressive strain the Si substrate induces in the Ge overlayer [37]. At 1 BL (2 ML) coverage a complete wetting layer forms. It is possible to grow very large domains of very uniform $5\times 5$ [54, 123]. The structure of $5\times 5$ was introduced in Sec. 3.8.

Ge grows in the Stranski-Krastanov mode, so growth proceeds layer-by-layer up to the critical thickness $\sim 3$ BL where tall 3D islands make their appearance [91]. These islands take two forms: tall, and flat [124, 29, 143]. The tall islands at 3 BL coverage are roughly 40 BL high and make up $\sim 60\%$ of the 3D island population. They are tapered prims, having $\{113\}$ side walls and flat tops that are largely strain relieved and exhibit mixed $2\times n$ reconstruction. The flat islands are $\sim 40\%$ of the population and $\sim 7$ BL high. They show long period undulations on the top faces indicating a network of dislocations at the substrate island interface. This network relieves some of the strain and the exposed reconstruction is $7\times 7$, intermediate between $5\times 5$ reconstruction found on the highly strained wetting layer and the $2\times n$ found on fully relaxed facets [143, 51].

With long annealing (30 min at 500°C) a new island form is found. These resemble atolls with tall wide rims, and a shallow interior. The reconstruction at the top of
the rim is $2 \times n$, while at the bottom of the lagoon it is $7 \times 7$. The hypothesis is that dislocations introduced at the perimeter of the tall islands, where the strain is highest, locally relieve that strain [124]. Thus the perimeter becomes a low strain region for adsorption and Ge diffusion takes place preferentially from the centre of the island, where the strain remains high, towards the edges [52], eventually leaving the interior depleted [29, 122].

5.4 Comparison between $5 \times 5$ and $7 \times 7$

5.4.1 Intermixing

The degree of substitution that takes place at temperatures $>100^\circ C$ has been the subject of debate. Early studies based on RBS [117] and AES [169] suggested that no intermixing took place and that an abrupt interface existed between the Si substrate and the Ge overlayer. MEIS results were more nuanced, indicating for 2 BL coverage, an abrupt interface at $<400^\circ C$, Ge-Si mixing within the interface BL at $T \sim 550^\circ C$ and complete mixing at $T \sim 770^\circ C$. For thicker films, the same behaviour was observed for the wetting layer, but the 3D islands were entirely Ge, even at the highest temperatures. STM measurements of adatom behaviour also suggested small intermixing for temperatures $<500^\circ C$.

However, the recent view is that intermixing takes place at all temperatures within what has been called the high temperature regime. The first, and most direct piece of evidence comes from filled state STM images which show variable adatom heights on the $5 \times 5$ wetting layer [54]. Since every adatom in the $5 \times 5$ F/UHUC is crystallographically equivalent this was taken as evidence for subsurface Si substitution within
the nominally Ge overlayer. The subtle changes in bond angle and length that come from Si intermixing leads to visible changes in the electron density measurable at the surface. This effect was seen for coverages at thicknesses up to 3 BL (the wetting layer limit) and temperatures as low as 350°C. Further studies by AFM confirm this finding [217]. So reconstructed Ge overlayers are always populated with Si. XAFS experiments on Ge samples annealed at 500°C have shown that 50% of the atoms in the 5×5 wetting layer are Si [24, 154]. Therefore, while the Si(111)7×7 surface is pure Si, the Si(111)-Ge5×5 one is a mixture of Ge and Si. However, for the sake of notational simplicity we will continue to refer to Si(111)-Ge5×5 even though the exposed surface is mixed species, as Ge5×5.

5.4.2 Diffusion

Studies of heteroepitaxial island growth on Si and Ge surfaces in both strained and unstrained states have demonstrated marked differences in diffusion rates for adsorbates [36, 37]. The goal was to identify the effect of four different parameters on the diffusion length of adsorbates. The parameters were: the adsorbate species, substrate species, substrate reconstruction, and substrate strain. These studies, surprisingly, found that the diffusion length for Si and Ge adsorbates was nearly identical on domains of 7×7 and 5×5 for Si(111)-Ge prepared by rapid deposition of Ge. So the substrate reconstruction did not play a significant role in determining the diffusion length. This was despite the fact that the 7×7 domains were covered with many HUCs occupied with magic clusters. On the other hand, there was a substantial difference in the diffusion length when Si is replaced with Ge for either the diffusing adsorbate, or the substrate species.
5.5 Solid Phase Epitaxy

Solid phase epitaxy (SPE) is the practice of seeding a surface with the adsorbate of interest in solid form, before annealing to release and order it. In its original form it was used for homoepitaxy and the solid source was generated by ion bombarding the surface to create an amorphous layer. In the heteroepitaxial form practiced here the adsorbate is delivered to the surface through molecular beam epitaxy, but the substrate is held at low temperatures to reduced diffusion. Thus the initial deposition is conducted well in the kinetic regime \( (F/D \gg 1) \). Since the critical cluster size \( i \) diminishes with the \( F/D \) ratio, this scheme serves to generate many nuclei.

Germanium SPE on Si(111)7×7 has indeed been demonstrated to yield higher Ge island densities [136, 177]. Sold phase epitaxy with a 400°C anneal was found to produce almost 4× higher island density than MBE conducted at the same temperature. Lower anneal temperatures are expected to yield higher island density. However, an effective floor is established by the minimum temperature necessary to overcome the kinetic barrier to DAS deconstruction. As discussed earlier, Ge deposition on Si(111)7×7 conducted at room temperature does not disrupt the stacking fault and dimer layers of the 7×7 reconstruction [56, 71]. The threshold has been found to be \( \sim 380°C \) [56].

5.6 Ge Surface Growth Procedures

This section describes the techniques developed and used by the author for growing the Ge surfaces which are central to this thesis. The preparation procedure begins
Figure 5.6: Ge Surface Preparation Techniques. a) In conventional high temperature MBE, Ge is deposited onto a hot surface. The result is very large domains of 5×5 with excellent order. b) The same procedure at lower temperatures yields many domains of 5×5 and 7×7 with triangular 7×7 islands. In SPE the Ge is first deposited onto a room temperature surface (c) and then annealed at low temperatures.
with the creation of Si(111) 7×7 according to the recipe described in 3.9. Germanium surfaces were grown by both MBE (deposition onto a hot substrate), and SPE (deposition onto a cold substrate followed by annealing). The results are summarized in Fig. 5.6. The top box shows the results for MBE conducted in two temperature regimes: 0.3 DCA and 0.75 DCA sample heating current corresponding to 650°C and 500°C (all temperatures are based on resistance thermometry and carry an uncertainty of ~ 30°C). In both cases, the nominal coverage, measured by thickness monitor, was 1 BL. The exposure time was 8 min and the anneal was continued for another 7 min afterwards for a total time at high temperature of 15 min. The high temperature procedure yields very large domains of high quality 5×5. The low temperature technique produces a surface with three layers: exposed 7×7 substrate, and first and second bilayer growth. The first bilayer contains domains of both 7×7 and 5×5, with 5×5 dominating, but the second bilayer is entirely 7×7. It is not clear why second layer growth is proceeding before first layer is complete, or why that growth is exclusively 7×7.

In the SPE method, shown in the bottom box of Fig. 5.6, Ge was deposited onto a room temperature substrate, and then annealed for 15 min. After the first step, the 1 BL overlayer is amorphous, although an FFT of the image (shown as an inset) shows strong spots with 7×7 periodicity, consistent with HUC confinement of the adsorbate. After annealing at 500°C for 15 min the surface reconstructs as 5×5. The triangular voids arise because the coverage was slightly less than the 1 BL target; in this case the true coverage is 0.87 BL. Smaller scale images reveal that the domains of 5×5 are relatively small and they are separated by well-ordered domain boundaries. Curiously, the reconstruction at the bottom of the voids is, in many places, 5×5. This
suggests substantial Si-Ge intermixing.

Figure 5.7 shows the differences between surfaces prepared by SPE conducted 500°C (b, c) and 550°C (a). Low temperature and low coverage (5.7b) generates isolated islands on top of a 7×7 reconstructed substrate. The island surfaces are reconstructed in a mixture of 7×7 and 5×5. The stoichiometry of each of the domains is unknown, but presumably it is a mixture of Ge and Si, rather than a pure species for either reconstruction. Figure 5.8 shows an even more unusual feature: an island of 9×9. At higher coverages (5.7c), second BL growth begins, and the number of 7×7 domains is greatly reduced. At higher temperatures (5.7a) the surface reconstructs exclusively as 5×5 with many domains separated by straight domain boundaries. One characteristic of second BL SPE growth at higher temperatures is the triangular areas of twinned 5×5 that can be found on some second layer islands and where steps have flowed over first layer growth below [72].

Relaxed, 3D islands of Ge can be grown by applying more than 2 BL of Ge in either an MBE or SPE process. Figure 5.9 shows the result of an SPE preparation of 15 ML of Ge followed by 7 min anneal at 575°C. The surface is covered with tall 3D islands of Ge. As seen in Fig. 5.9b, the tops of some are reconstructed as 7×7, others 2×n, and the wetting layer 5×5.

5.7 Summary

This chapter reviewed the principles of surface growth. The phenomenon was approached from the perspective of the motion of individual atoms, and that of a thin continuous film. The former discussed the important interplay at work between thermodynamics and kinetics. The latter introduced the role of strain and its effect on
Figure 5.7: Solid Phase Epitaxy Phases. a) SPE conducted at 550°C consistently yields 5×5 domains. Near step edges small twinned domains, characteristic of 2nd BL growth [72], can be found. b) SPE at 500°C and sub-BL coverage gives islands of mixed 7×7 and 5×5 over a 7×7 substrate. c) On the second BL the number of 7×7 domains diminishes.
**Figure 5.8: An Island of 9×9.** Ge grown by low temperature SPE with a coverage of 0.03 BL, and short, 10 min, anneal. The larger island contains ~10 HUCs of 9×9. The domain boundary of the 7×7 substrate on which the island nucleated may be responsible for the unusual reconstruction.

**Figure 5.9: 3D Islands of Ge.** a) Large scale islands of Ge prepared by SPE with 7.5 BL of Ge and a 7 min anneal at 575°C. b) Closeup of two islands and the substrate below, taken from the region highlighted by the box in a. The wetting layer below is 5×5, the island on the left is 7×7, and the island to the right is 2×n. The colour scheme has been adjusted to provide contrast to all three surfaces simultaneously. c) Line profile through islands shown by the line in a.
growth modes, particularly the Stranski-Krastanov mode which will be so important for this work. The focus of this chapter was the growth of Ge on Si(111)\(7\times7\), and a detailed examination was made of the phase diagram for this system. Also explained, was the technique of solid phase epitaxy which manipulates the thermodynamic/kinetic balance to encourage the growth of small islands in many domains. Finally, the details of the surface preparation routines for Ge\(5\times5\) that will be used in the remaining work was presented.
Chapter 6

Magic Clusters

Early in its existence, surface science was focused on the study of periodic 2D surfaces that were either relaxed or reconstructed. With the excitement surrounding nanoscience, and armed with local probes like the STM, there has been a subtle shift recently to investigate systems that are aperiodic. There is particular interest, for both practical and fundamental reasons, in the study of nanoclusters: small features generated by the atomic scale coalescence of adsorbates. This chapter will review the past work on magic clusters, a special class of nanoclusters marked by an extremely high standard of regularity. A recent, comprehensive review of magic clusters is available in Ref. [200].

6.1 Clusters

We will start by exploring the different types of cluster found on surfaces. We restrict ourselves to small multi-atom features whose lateral extent is less than a few reconstruction unit cells. Figure 6.1 shows a schematic of possible cluster size distributions.
Fig. 6.1: Cluster Dispersion. Schematic of scales of cluster dispersion. From monodispersed to polydispersed clusters. Identical monodispersed nanoclusters are described as magic.

Fig. 6.1a shows a collection of monodispersed clusters - every cluster is identical to every other one. Compare the clusters in Fig. 6.1b where there are two distinct species - the size distribution is bicameral and the clusters are bidispersed. Finally Fig. 6.1 shows a polydispersed system where all clusters are a different species. In these examples the variable of interest is cluster size, but it could just have easily been composition or structure.

Clusters that show preferred structures, like those in Fig. 6.1a & b are called magic clusters. The name descends from nuclear physics where nuclei containing special numbers of nucleons are unusually stable. 3D homoatomic nanoclusters also show stable sizes at magic numbers corresponding to closed electronic shells. The same effects at work on a surface make it possible to grow perfectly monodispersed 2D clusters where every cluster has identical structure. However, there are degrees of “enchantment” and the term magic is applied even when there are a variety of observed cluster configurations, so long as the variety is restricted (e.g. 6.1b). On a reconstructed surface two forces can play a role in stabilizing clusters at magic sizes.
The first is the saturation of dangling bonds, the same effect that drives 3D clusters towards magic sizes [93, 23]. The second important factor is the role of the substrate in confining cluster growth [200].

Figure 6.2 demonstrates these two factors at work. Ga on Si(111)-Ga$\sqrt{3} \times \sqrt{3}$ (Fig. 6.2a) forms magic clusters containing 3, 6, 10, 15... Ga atoms [97, 98, 200]. These cluster sizes are dominant because they represent local minima in the number of dangling bonds. However, there is no clear-cut thermodynamically imposed limit to the maximum size. On the other hand, for Ge clusters grown on Si(111)7$\sqrt{7}$ (Fig. 6.2b), there is no one dangling bond minimizing structure [6]. However, the accessible bonding sites are restricted to the centre of the unit cell, so many different cluster species form, but their positions and maximum size are restricted by the substrate reconstruction. The case of Ga on Si(111)7$\times$7 (Fig. 6.2c) marries the two effect: a six atom Ga cluster minimizes the number of dangling bonds and fits neatly within a 7$\times$7 HUC. Fewer atoms would leave unsaturated dangling bonds, and more atoms extend beyond the HUC. Thus, for this system, six atom Ga clusters are found almost exclusively, and larger and smaller species are eliminated. Also, since the location of each cluster is defined by the reconstruction, a surface where every HUC contains a cluster becomes a lattice of cluster (also known as a nanocluster array). Thus, careful matching of the adsorbate and substrate makes it possible to create a perfect 2D crystal of atomically identical objects.

6.2 Basins of Attraction

In 1998 Cho and Kaxiras published an influential paper titled ”Diffusion of adsorbate atoms on the reconstructed Si(111) surface” [38]. Using careful DFT modeling they
Figure 6.2: Magic Clusters. a) Ga on Si(111)-Ga $\sqrt{3} \times \sqrt{3}$ forms magic clusters of preferred, but various, closed shell sizes [200] (reprinted with permission from Taylor & Francis). b) Ge clusters on Si(111) are confined to 7×7 HUCs, but lack well defined structures [6] (reprinted with permission from Elsevier). c) The combination of dangling bond saturation and HUC confinement leads to monodispersed Ga clusters on Si(111)7×7 [100] (reprinted with permission from the American Physical Society). d) At higher coverages, the reconstruction patterns the clusters into a 2D lattice [86] (reprinted with permission from the American Physical Society).
investigated the binding energies of adsorbates of valence 1-4 (K, Mg, Ga, Ge) on a fragment of the 7×7 unit cell. Up to that point conventional wisdom, driven by coordination arguments, held that adatoms were expected to adsorb atop an adatom or restatom to saturate the partially filled dangling bond there. Instead, the authors found that for all adsorbates the sites atop the restatoms and adatoms were unstable high-energy positions. In fact, the adsorbate atoms energetically prefer the high-coordination sites adjacent to the restatoms. The annular locus of low energy sites defines what Cho and Kaxiras described as a basin of attraction surrounding the restatom. Diffusion within the basin is facile but diffusion between basins is difficult. At room temperature, the ratios of intra- to inter-basin hopping events for K and Ga are ∼10^2 and ∼10^3 respectively.

The basins of attraction demonstrated by Cho and Kaxiras’ suggest a mechanism for cluster formation based on filling the basins around each restatoms in a DAS HUC. But since the barrier to diffusion within the basin is small, the adsorbate, at room temperature, is in constant motion, and so the structures that form might be better described as confined dynamic features. An obvious distinguishing characteristic of these features is that they image as enhanced restatoms, and so they appear as triangular features pointing in the same sense as the HUC in which they are contained.

### 6.3 Al, Ga, In

The archetypal magic clusters on 7×7 are those formed by Al, Ga, and In. As we shall see, they are distinguished by the structural perfection of the individual clusters, and the perfection with which lattices of many clusters can be grown. Glimpses of Al magic clusters were in evidence as early as 1993 [220], but recognition of their
significance waited until 2001 when, in close succession, In [218], Ga [100] and Al [94, 86] magic clusters were discovered. They each share a common structure, which is shown schematically in Fig. 6.3. It consists of three nested equilateral triangles within HUC. The largest triangle is defined by the three corner adatoms. The second, half the size of the first and oriented in the opposite sense, is made of six adsorbate atoms: three at the corners and three along the edges. The third triangle lies within the second and is defined by the three Si edge adatoms. An important structural feature is that these Si edge adatoms have been displaced from their regular $T_4$ sites towards the centre of the HUC to atop $T_1$ sites. The three corner metal atoms take the place of the Si edge adatoms at $T_4$ sites where they are bonded to two restlayer atoms and a Si adatom. The three edge metal atoms are bonded to what were the restatoms, and two Si adatoms. The displaced Si adatoms make their fourth and final bond with restlayer atoms below. This structure, whose elegance arguably rivals $7\times7$
Figure 6.4: Magic Cluster HUC Preference  Al, Ga and In magic clusters all prefer FHUC occupation for initial coverage. At higher coverages their behaviors diverge; for Ga the preference disappears quickly, for In it is maintained to the point where all FHUCs are full, and only UHUC remain available, Al lies in between. Adapted from Ref. [200].

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itself, succeeds in reducing the number of dangling bonds in a HUC from 9 (for 7×7 without adsorbate, and ignoring the corner hole) to only the 3 on the corner adatoms. This especially effective dangling bond saturation leads to high cluster stability and excellent monodispersion; with proper preparation they are essentially ideal magic clusters [100]. Occasionally they are referred to as Me₆Si₃ to emphasize the similarity with the electronically mediated stability and stoichiometric consistency of molecules. This model has been verified with ab initio calculations for In [103][86], Al [86], and Ga[32][86]. For the case of Ga, the model has further corroboration from dynamical LEED [32] and RHEED [135].
### Table 6.1: Magic Cluster Statistics

A comparison of the properties of Al, Ga, and In magic clusters. The preparation columns give the optimal deposition rate and annealing temperatures for preparing clusters [86]. The stability columns give the maximum observed survival temperatures and the calculated binding energy for a complete-coverage unit cell. Also given is the energy difference for faulted vs. unfaulted formation $\Delta E_B$ based on calculation and observations of occupancy differences. For Al and Ga the experimental values are only valid for very sparse coverages.

<table>
<thead>
<tr>
<th>Element</th>
<th>Preparation</th>
<th>Stability</th>
<th>$\Delta E_B$ F/UHUC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ML/min)</td>
<td>(°C)</td>
<td>(eV/UC) (eV)</td>
</tr>
<tr>
<td>Al</td>
<td>0.01</td>
<td>500-600</td>
<td>-25.6</td>
</tr>
<tr>
<td>Ga</td>
<td>0.02</td>
<td>400-500</td>
<td>-22.3</td>
</tr>
<tr>
<td>In</td>
<td>0.05</td>
<td>300</td>
<td>-19.7</td>
</tr>
</tbody>
</table>

#### 6.3.1 HUC Preference and Cluster Lattices

For all three species the preferred cluster site is within the faulted, rather than unfaulted HUC. At low cluster densities, for all of the species, the majority of clusters are found in the FHUC. However, the strength of that preference varies between the species, as shown in Fig. 6.4. In clusters show remarkable affinity for the FHUC exhibiting essentially exclusive occupation of that HUC up to 0.12 ML, the point where they are all filled, known as half-covered [86, 87]. On the other hand, Ga clusters show FHUC preference only for only low coverages. Aluminum falls somewhere in between; it’s preference decays quickly with cluster density, but remains tilted in favour of the FHUC right up to full-coverage. On a fully covered surface (0.24 ML) every HUC contains a cluster which together form a periodic 2D lattice of clusters with a pitch and position defined by the $7 \times 7$ unit cell [87, 104, 105, 196, 218, 224]. The full-covered lattice has honeycomb symmetry (if the substrate is ignored), and the half-covered surface is a triangular lattice.
6.3.2 Preparation

Magic clusters are prepared by simply depositing the adsorbate onto a previously prepared Si(111)7×7 surface held at a moderate temperature. Alternatively, the adsorbate can be deposited onto a room temperature substrate and then annealed for a few seconds. The crucial parameter is the substrate temperature, rather than the sequence of operations. The optimal preparation temperature for cluster formation is shown in Table 6.1 and increases with decreasing atomic number. The same trend is observed for cluster stability, measured by the temperature at which clusters begin to disintegrate and other, lower energy, phases form.

Several early reports [103, 86] emphasized the need for low deposition rates — the values in Table 6.1 are reported to be optimal. The rational was that metal adatoms required sufficient time to diffuse about the surface, find an incomplete cluster, and bond to it before the arrival of succeeding adatoms. Higher substrate temperatures speeds up the process, but the transition to a lower energy phase (e.g. $\sqrt{3} \times \sqrt{3}$) establishes an upper temperature limit. The alternative is to keep the flux rate low (~0.01 ML/min). Although this picture is rational, many workers have reported excellent cluster growth for Al [85], Ga [100, 196] and In [218] clusters using the opposite technique — deposition onto a cold substrate followed by annealing — or high rate deposition onto heated substrates (>0.1 ML/min). These results suggest that the clusters are kinetically robust.

6.3.3 Substitution

Aluminum exhibits significant substitution for Si adatoms [87, 105, 94, 129]. In fact, it passes through three distinct stages with increasing coverage: low coverages of Al
mainly substitute for corner and edge Si adatoms. Once the coverage reaches a threshold of \(\sim 0.07\) ML magic clusters begin to form. The substitution of corner adatoms remains the same, but the edge adatom substitution decreases since edge adatoms are involved in cluster formation. In the third stage, as the surface approaches cluster saturation, the number of corner adatom substitutions starts to grow again. The net result is that at high Al coverages, the large number of displaced Si adatoms coalesce into islands [94]. For Ga clusters, STM [135], RHEED [135] and LEED [31] show that Ga also substitutes for \(\sim 40\%\) of Si corner adatoms. On the other hand, In only shows evidence for substitution after annealing at temperatures approaching the stability limit [158].

### 6.3.4 STM, Electronic Structure, and Calculations

Because they are aperiodic, essentially all of the experimental studies on magic clusters have been made with STM (the two exceptions are investigations with LEED [32] and RHEED [135] on periodic cluster arrays). STM images of the clusters are shown in Fig. 6.5. In empty state images (b,d,f) the clusters appear as distinct six atom triangles, in filled state images at high bias (a,c) they show up as compact three atom triangles, and at lower bias (e) appear as a depression containing week three-fold features. The empty state images of Al and Ga show brighter intensity on the three edge atoms of the cluster, while the In cluster shows brighter intensity on the clusters’ corner atom, leading to an open appearance. The straightforward interpretation of the three filled state bumps and the six empty state protrusions corresponding to the three Si and six metal atoms respectively has been confirmed by \textit{ab initio} calculations [103, 86, 32, 224]. Interestingly, calculations show that the bright corner atoms in
Figure 6.5: STM Images of Al, Ga, and In Magic Clusters taken from the Literature. a & b) show Al [94], c & d) Ga [135] nanocluster arrays with one cluster in every HUC. e & f) show five isolated In clusters [103]. Filled state images are shown on the left, and empty state on the right. All images reprinted with permission from the American Physical Society.
CHAPTER 6. MAGIC CLUSTERS

Table 6.2: Magic Cluster Charge Transfer. Counting the number of electrons before and after charge transfer for a clean 7×7 unit cell and unit cells with 1 and 2 magic clusters. In all cases the number of adatom electrons is 5, but since the number of adatoms sharing those electrons diminishes the density goes up (last column).

<table>
<thead>
<tr>
<th>Surface</th>
<th>Electrons Before</th>
<th></th>
<th>Electrons After</th>
<th></th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH</td>
<td>RA</td>
<td>AA</td>
<td>Total</td>
<td>CH</td>
</tr>
<tr>
<td>7×7</td>
<td>1</td>
<td>6</td>
<td>12</td>
<td>19</td>
<td>2</td>
</tr>
<tr>
<td>7×7 + 1 Cluster</td>
<td>1</td>
<td>3</td>
<td>9</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>7×7 + 2 Clusters</td>
<td>1</td>
<td>0</td>
<td>6</td>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>

As seen in Sec. 3.6, the electronic structure of 7×7 near the Fermi level is dominated by the adatom dangling bonds, which after charge transfer, are populated by 5 electrons. The addition of a single cluster saturates the bonds on three restatoms and three edge adatoms leaving dangling bonds on 1 corner hole, 3 restatoms, and 9 adatoms. Charge transfer to the corner hole and restatom dangling bonds leaves 5 electrons to be distributed among the 9 remaining adatoms. For the case of two clusters (one in each HUC) the number of adatom electrons is the same. Table 6.2 compares the values for the three cases. Surprisingly, the number of electrons in the adatom bands is unaffected by the number of clusters in the unit cell. Ab initio calculations have been performed for In clusters at half-coverage and Al clusters at full coverage which correspond to 1 and 2 clusters per unit cell [224]. They demonstrate that clusters open a gap between the adatom bands at the Fermi level of 0.1 eV for In clusters and 0.2 eV for Al. They also noted that in the case of half-coverage, surface conduction can proceed by diffusion through channels connecting the unoccupied
UHUCs. When the surface is fully-covered the channels are eliminated, electron density near the Fermi level is restricted to the rings of corner adatoms, and conduction can only occur by tunneling from ring to ring.

For the bands associated with an Al cluster itself there is a large gap, consistent with its closed shell electronic structure. With UPS the gap has been measured to be >0.5 eV [227], and with STM 1.7 eV (once tip induced band bending is eliminated), theory predicts a gap of 0.6 eV [223]. The discrepancy is attributed to the well known tendency for LDA calculations to underestimate band gaps. Other works have confirmed the semiconductor nature of In [219, 103] magic clusters

6.4 Other Magic Clusters

The Group 13 elements represent a pinnacle of sorts for magic clusters: they have the best monodispersity, registration, and stability. Not surprisingly then they are the most studied. However, magic clusters form for many other species. Figure 6.6 shows a selection of structures of magic clusters grown on Si(111)7×7. The accompanying table summarizes some statistics and provides references.

None of the clusters display the same almost ideal uniformity exhibited by the Group 13 elements. For example, Pb produces examples of what have been called “borderline” magic clusters. The ideal cluster is shown in Fig. 6.6; because Pb is a Group 14 species, dangling bonds remain on this cluster. The term borderline derives from the narrow temperature range for preparation (±20° C), and most interestingly in the diverse, but systematic assortment of clusters that form outside of that temperature range. The reason for this is not thermodynamic, the 6 atom cluster is more than 900 meV more favorable than the nearest variant, but kinetic. For Pb clusters,
Figure 6.6
**Figure 6.6: Other Magic Clusters.** Structures and statistics for selected magic clusters grown on Si(111)7×7. For each cluster type the table shows the number of metal atoms, and the change in Si adatoms. Structures that have been verified by calculations are marked with asterisks, and the reference marked likewise.

<table>
<thead>
<tr>
<th>Element</th>
<th>Structure</th>
<th>Me</th>
<th>Δ Si</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Ga/In</td>
<td>Fig. 6.3*</td>
<td>6</td>
<td>0</td>
<td>103*[86]*…</td>
</tr>
<tr>
<td>Co</td>
<td>a*</td>
<td>6</td>
<td>0</td>
<td>232*, [233]</td>
</tr>
<tr>
<td>Cu</td>
<td>b</td>
<td>6</td>
<td>0</td>
<td>226, 234</td>
</tr>
<tr>
<td>K</td>
<td>?</td>
<td>6</td>
<td>?</td>
<td>207</td>
</tr>
<tr>
<td>Mn</td>
<td>c</td>
<td>7</td>
<td>0</td>
<td>194, 195</td>
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<td>a</td>
<td>6</td>
<td>0</td>
<td>195</td>
</tr>
<tr>
<td>Na</td>
<td>e*</td>
<td>6</td>
<td>0</td>
<td>208*, [1]</td>
</tr>
<tr>
<td>Pb</td>
<td>d</td>
<td>6</td>
<td>0</td>
<td>106*</td>
</tr>
<tr>
<td>Tl</td>
<td>f</td>
<td>15</td>
<td>-6</td>
<td>192, 102, 235</td>
</tr>
<tr>
<td>Tl</td>
<td>g</td>
<td>5</td>
<td>+7</td>
<td>235</td>
</tr>
<tr>
<td>Tl</td>
<td>e</td>
<td>6</td>
<td>0</td>
<td>235</td>
</tr>
</tbody>
</table>
the remaining dangling bonds conspire to capture diffusing Pb adatoms before they have a chance to form stable clusters.

6.5 Summary

The concept of surface magic clusters has been briefly reviewed. In particular the behaviour of the exceptionally uniform magic clusters that grow from the Group 13 elements Al, Ga, and In has been examined: their atomic and electronic structure, stability, and ability to form lattices. In future chapters magic clusters will be investigated on the Ge $5\times5$ surfaces and at the boundaries between $5\times5$ domains.
Chapter 7

7×7 Domain Boundary

Background

The 7×7 DAS reconstruction was discussed in Ch. 3. There it was seen that 7×7 domains form during a high temperature transition from 1×1. Where those domains meet, a boundary will form between them. This chapter will review the existing literature on those 7×7 domain boundaries. Subsequent chapters will discuss the symmetries of domain boundaries on DAS, examine the detailed atomic structures of new 5×5 boundaries, and discuss the properties of networks of such boundaries with reference to the physics of foams, and grain growth.

7.1 Reconstruction Domain Boundaries

Real surfaces, even with careful preparation, inevitably include defects; areas where the crystalline periodicity is broken. A zero-dimensional (0D), point defect can take the form of a vacancy, where an atom is absent; impurity, where an atom of a different
A boundary can be broadly categorized according to the relationship between the domains that define it as a) mixed domain phases, b) shifted domains, c) rotated domains, d) reflected domains.

Examples of two-dimensional (2D) defects are islands of second layer growth and domains of different phase. If the island height becomes large it can be regarded as a three-dimensional (3D) defect. The most common and often discussed one-dimensional (1D) defect is the step, where an additional layer of material is built upon the layer below. The structure of steps, their interaction with one another, and their important role in growth have been intently studied by surface science [84].

Another type of one dimensional defect arises at surfaces: domain boundaries (2D grain boundaries, or domain walls). These are not to be confused with the boundaries of 3D grains in a polycrystalline sample that intersect the surface [156]. Generally these are avoided by using single crystals with well-defined surfaces. Instead, domain
boundaries arise from the fact that there are different ways that a surface reconstruction can be registered with the bulk substrate. The surface ordering proceeds through a sequence of nucleation followed by growth. Around each nucleus, the domain that forms places every unit cell in registration with the ones around it. The translational symmetry proceeds unbroken, directed by registry with the substrate below and alignment with the preceding unit cells. However, where adjacent domains come together there is likely to be misfit between the cells where they meet. The different relationships that can exist between the two domains are summarized in Fig. 7.1 and define the nature of the boundary between them. Domains are mixed if they are of different phases, whether ordered or amorphous. In cases where domains are of the same ordered phase then they can be misfit through the plane isometries: translation, rotation, and reflection subject to the constraint of registration with the bulk. The boundaries between these domains can be referred to as phase or anti-phase, tilt, and twin boundaries respectively.

Table 7.1 lists a selection of reconstructed surfaces for which domain boundaries have been observed. The examples include physisorbed noble gas solids, spontaneous and adsorbate induced reconstructions on metal and semiconducting surfaces, and molecular overlayers. The table includes cases of each of the domain boundary types illustrated in Fig. 7.1.

Our interest lies mainly with boundaries between domains of 5×5. The symmetries of the DAS reconstruction and substrate registration restrict domains to being misfit through translation alone; tilt and twin boundaries are forbidden. The only

\footnote{\textsuperscript{1}This picture of domain boundaries arising from the independent nucleation is suitable for most situations. However, in the cases of Noble gases on graphite \cite{58, 191} and the Au herringbone reconstruction \cite{11, 128} the domain boundaries form for strain relief. In the former case the domain boundaries raise the energy, in the latter they lower it.}
<table>
<thead>
<tr>
<th>System</th>
<th>Mixed</th>
<th>Rotated</th>
<th>Shifted</th>
<th>Reflected</th>
<th>References</th>
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<tr>
<td>Clean Metal Reconstructions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au(111)√3×23</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td>[128], [11]</td>
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<td>Au(110)2×1</td>
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<td></td>
<td></td>
<td></td>
<td>[155]</td>
</tr>
<tr>
<td>Pt(111)</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td>[25][77] [148]</td>
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<tr>
<td>Noble Gases on Graphite</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td>[58]</td>
</tr>
<tr>
<td>Xe√3×√3</td>
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<td>X</td>
<td></td>
<td></td>
<td>[88][191]</td>
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<td>X</td>
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<td></td>
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<td>Adsorbate Covered Reconstructions on Metals</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td>[20]</td>
</tr>
<tr>
<td>Cu(100)-Fe2×2</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>[42]</td>
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<td>Clean Semiconductor Reconstructions</td>
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<td>Si(111)1×1/5×5/7×7</td>
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<td>[44, 45]</td>
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<td>Ge(100) 2×1 + c4×2</td>
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<td></td>
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<td>[221]</td>
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<td>X</td>
<td></td>
<td>X</td>
<td></td>
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<td>Ge(110)c8×10</td>
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<td>[82]</td>
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<td>Si(111)7×7</td>
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<td>X</td>
<td>X</td>
<td></td>
<td>[65] [168]</td>
</tr>
<tr>
<td>Si(111)7×7 + Au5×2</td>
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<td></td>
<td></td>
<td></td>
<td>[99]</td>
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<td>Si(111)-Ga6.3√3×6.3√3</td>
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<td></td>
<td></td>
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<td>[2][161]</td>
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<tr>
<td>Si(111)-Ag√3×√3 IET</td>
<td>X</td>
<td></td>
<td>X</td>
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<td>[120][127]</td>
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<tr>
<td>Si(111) Ag√3×√3 HCT</td>
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<td></td>
<td>[43]</td>
</tr>
<tr>
<td>Co/Si(111)-Co√7×√7</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td>[92]</td>
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<td>Ni/Si(111)-Ni√19×√19</td>
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</tr>
<tr>
<td>Au/Si(111)-Au√3×√3</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>[126][133]</td>
</tr>
<tr>
<td>Tl/Ge(100)-Tl2×1</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td>[160]</td>
</tr>
<tr>
<td>Molecular Monolayers on Graphite</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>succinic acid</td>
<td></td>
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<td>X</td>
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<td>[80]</td>
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<td>didodecylbenzene</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>[153]</td>
</tr>
<tr>
<td>2-pyridone</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>trimesic acid</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td>[96]</td>
</tr>
<tr>
<td>terephthalic acid</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td>[96]</td>
</tr>
</tbody>
</table>

Table 7.1: Observations of Domain Boundaries. A partial collection of domain boundaries observed in real systems.
example of 5×5 domain boundaries found in the literature is in Ref. [45], which looked at the metastable Si(111)5×5 phase that forms as an intermediate step as 2×1 is annealed into 7×7. On the other hand, there is a substantial body of literature on the Si(111)7×7 DAS reconstruction. The rest of this chapter is devoted to exploring that body of work.

7.2 First Observations of 7×7 Domain Boundaries

Since domain boundaries are an inherently aperiodic features, that are rare in well-ordered samples, they are unsuitable for study with the diffraction techniques that dominated surface science until the early 1980s. That decade marked the advent of microscopes that were sensitive to surface features on the scale of nanometers. Domain boundaries of 7×7 were first imaged in 1980 using reflection electron microscopy (REM) before the DAS structure of 7×7 had even been proposed [132, 181]. They were next observed in LEEM [182, 14, 159]. Neither of these techniques has the resolution necessary to image the arrangement of atoms at the boundary. But through contrast inversion it was observed that a boundary was present, and at high temperatures it was possible to watch its formation.

The first atomic scale observations of domain boundaries were made by Demuth et al. at IBM in 1986 [39]. In a paper demonstrating a new STM design, they presented an image that contains a well-resolved domain boundary, albeit one that is irregular and contaminated. They did not provide a measurement of the shift between the domains. They did, however, note that for well-prepared samples defects like domain boundaries occur only vary rarely. Images of a domain boundary also appeared, almost incidentally, in a paper on STM image analysis by Berghaus et al. [19].
The first report to focus exclusively on domain boundaries was from Sumita \textit{et al.} [173]. They used STM to examine in detail the structure of a single uniform domain boundary. They found that it stretched across a terrace from step edge to root, they measured the size of the boundary unit cell, and measured the misregistration between the two domains. In another first, they also put forward a structure by applying a lattice gas model in which their building blocks are \(2 \times 2\) subunits centred on an adatom.

## 7.3 The Origin of Domain Boundaries

In the early REM measurements, that first reported DAS domain boundaries, domains were watched as they grew out of disordered \(1 \times 1\) [132, 181]. Boundaries were formed where out of phase \(7 \times 7\) domains met one another. LEEM studies showed the same process [182, 14, 145], but also found that when the density of nucleation points was reduced through the adsorption of residual gas, the number of domain boundaries was also decreased [14, 13]. This idea, that domain boundaries are formed by the intersection of domains that nucleate independently and out of phase, remains the standard explanation for their origin, although there have been counterclaims proposed [62].

## 7.4 From defects to regularity

Early in the \(1 \times 1 \rightarrow 7 \times 7\) transition, domains of ordered \(7 \times 7\) are separated by channels of \(1 \times 1\) [132, 181, 182, 14]. As the transition proceeds and the domains become more numerous, and grow in size, these amorphous channels become narrower. Ideally the
anomalous region between the two normally ordered 7×7 domains becomes atomically small (roughly the width of a unit cell) and assumes order of its own, subject to the boundary conditions imposed by the surrounding domains. These are the types of domain boundaries that are pertinent to this thesis. This concept, that boundary defined by atomically ordered domains should be atomically ordered itself, is one that will be returned to repeatedly.

Suboptimal preparation leaves channels between the domains spanning several unit cells and retaining 1×1 disorder. This can be achieved deliberately by maintaining the sample at a temperature just below the 1×1 →7×7 transition temperature where something akin to “edge melting” keeps the domain boundaries in the “liquid” 1×1 phase [46]. This effect is used to practical effect by REM, LEEM, and SEM observations which are resolution limited and unable to resolve atomic-scale boundaries between 7×7 domains [159, 3]. For these techniques, boundaries are only visible when they include the 1×1 disorder introduced by “edge melting”. Contrast at room temperature can be enhanced by decorating the boundaries with islands of an adsorbate like Ge [73, 78].

Examples of STM images of 1×1 boundaries appear in Refs. [121] and [231]. But STM does not suffer the same limited resolution as LEEM or SEM and can easily image domain boundaries which are atomically narrow and not amorphous. Again, these are the boundaries that are of interest here. It is important to note that STM and electron microscopy techniques are observing quite different things. The electron microscopies are imaging wide amorphous boundaries under high temperature dynamical conditions. Room temperature STM on the other hand, if samples are prepared appropriately, is viewing the static endpoint of preparation that results in
atomically narrow, and well-ordered, domain boundaries.

At the atomic-scale, domain boundaries express order at two scales: through the straightness of its trajectory and the uniformity of the atomic arrangement along its length. Clearly the best ordered domain boundaries are the ones that are both straight, consisting of a single segment, and uniform, with an atomically identical repeating unit cell. The earliest atomically-resolved domain boundaries were neither straight nor uniform [39, 19]. Their course was erratic and they were decorated with irregular protrusions. The first truly straight boundaries were reported in Ref. [173] and [62]. However, the general rule has been for short segments and disordered unit cells. The unofficial record is a single straight boundary with 12 atomically identical unit cells that spanned an entire 35 nm terrace [202].

### 7.5 Domain Boundaries and Step Structure

Almost all the studies in the literature have investigated domain boundaries found on otherwise well-ordered 7×7 terraces. These boundaries are all well isolated from one another, and supported at either end by the steps that bound the terrace. Exceptions can be found in Ref. [45] where a network of 5×5 domain boundaries produced from transformed Si(111)2×1, and Ref. [182] which saw networks of 7×7 domain boundaries from quenched 1×1. In both cases, the high density of nucleation sites, or reduced critical cluster size, resulted in a high domain density.

The isolated domain boundaries most often reported in the literature [182, 14, 145] propagate roughly perpendicular to the steps that define the terrace, and in fact have an important influence on the step morphology. For Si(111)7×7, step edges are largely confined to propagate along the easy ⟨101⟩ directions. The step energy
is dominated by their total length. Factors like whether the steps are composed of many short segments or few large ones (i.e. kink energy); or the interaction between the steps at the top and bottom of a terrace (step-step interactions) are expected to be of secondary importance. Domain boundaries cost energy, so the surface adapts to reduce their length by as much as possible. This is accomplished by having longer step edges and arranging the zigzags of adjacent steps so that they are counter-phase with one another. Longer segments makes the amplitude of the step undulation larger in the perpendicular direction. Matching the phase of neighbouring steps aligns the projection of one with the trough of the other. The result is that where the step above protrudes and the step below intrudes the terrace between them is very narrow. This is where the domain boundaries are found, because their lengths, and energies, are minimized [180]. The steps don’t zigzag because of the domain boundaries (as was proposed by Ref. [181]), they do so because the offcut direction is not aligned with the easy step directions. What domain boundaries do is amplify and align the zizags.

7.6 Domain Boundary Networks

The studies listed in the previous section dealt with isolated domain boundaries that cross a terrace connecting the upper step with the lower one. Domain boundaries have also been observed as complex networks where no one boundary traverses the terrace. For instance Ref. [45] observed a network of 5×5 domain boundaries produced from transformed Si(111)2×1 and Ref. [182] saw networks of 7×7 domain boundaries from transformed 1×1.

Phaneuf et al. [145], Hibino et al. [70], and Aizawa and Homma [3] studied domain boundary networks, the first two with LEEM and the third SEM. Phaneuf is clearly
observing 1x1 domain boundaries, and sees no anisotropy. Hibino explicitly states that they are observing 1x1 domain boundaries, but they do see anisotropy.

### 7.7 Nomenclature

#### 7.7.1 Itoh

The first systematic survey of DAS domain boundaries was undertaken by Itoh et al. in 1993 [83]. Several important points were made in this work that were either overlooked or left unsaid in previous works. First, they explicitly point out that a domain boundary consists of two normally ordered (NO) regions sandwiching an anomalously ordered region between. Since the bounding domains are ordered, the anomalous region between them is expected to be ordered itself, albeit in a different way than the NO regions which flank it. Thus, uniform domain boundaries are expected, rather than exceptional.

Most importantly, they recognized, and explicitly pointed out that, because of substrate registration, the shift between two domains must be discrete and is limited for 7x7 to only 48 possibilities. They introduced the phase shift vector (PSV) to identify the misfit between two domains. They offered two ways to express the phase shift vector. In the first scheme, the PSV is written as a linear combination of the 1x1 basis vectors $a_1$ and $a_2$. So two domains that have been shifted by $n \times a_1$ and $b \times a_2$ are simply written as $(n,m)$. In the second scheme, the phase shift between domains is broken into components that are parallel and perpendicular to the boundary. The authors pointed out that reflection symmetry is present for six of the phase shifts and that half of the remaining 42 shifts are related to the other half by reflection.
As a means for identifying the shift between two domains, Itoh’s scheme is unambiguous. But as a convention for labeling domain boundaries it is only useful when supported by three assumptions that are not made clear in the original paper. First, it assumes a domain boundary that runs in the [10\bar{1}] directions, along the short diagonals of the unit cell. Second, it requires a consistent scheme for orienting the basis vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) in one of the three crystallographically equivalent directions, in the presence of the domain boundary. Finally, it assumes that for a given phase shift vector, the boundary will adopt only one atomic configuration. The reasoning for this last point is that once one has specified the boundary direction, the phase shift between the domains, and the atomic arrangement of the normally ordered regions, then the boundary conditions for the problem are completely defined. So, absent degenerate solutions, the structure of the boundary will adopt a unique lowest energy configuration. Put another way, a boundary with one label will look the same as another boundary with the same label.

In this work, we will use Itoh’s first scheme, which expresses the phase shift in terms of the hexagonal unit vectors, although some important refinements will be made to solidify the assumptions discussed above. This will be discussed at greater length in section 8.1.2.

### 7.7.2 Zhao

A related scheme was introduced by Zhao et al. which attempted to encode information on atomic structure of the boundary within the label itself [230]. The system uses a three index notation which measures the shift of the two domains relative to one another and the boundary itself. The extra index defines a line of division beyond which
the order of each domain does not intrude, and effectively measures the width of the domain. In essence this scheme addresses boundaries ignored by the third assumption of the Itoh labeling; those that are not a local minimum. It’s claimed utility is in the treatment of domain boundaries grown far from thermodynamic equilibrium. But in these cases it’s labelling is unclear since such boundaries are not uniform. If the structure is not defined by the boundary conditions, then simply specifying another, in the form of the width, does nothing to clarify the structure.

### 7.7.3 Structural Models

The structure of uniform domain boundaries has been proposed for several different boundary types based on STM images. Since boundaries include large unit cells there have not, as yet, been any *ab initio* calculations on realistic boundary unit cells. Nevertheless, structures have been posited based on a selection of building blocks taken from the DAS motifs. The general measure of goodness for the proposed structures is the degree of agreement with STM images. The most important clue for this comparison are the locations of the adatoms which are always distinctive in empty state imaging. The principle concern was to minimize the number of dangling bonds. The same ideas will be adopted for the analysis in Ch. 9.

Sumita *et al.*, in the earliest report of a regular domain boundary, proposed a structure composed of 2×2 blocks centred on a DAS adatom [173]. They did not, however, attempt to account for the detailed atomic structure of the boundary. Hadley and Tear proposed the first atomic model of a domain boundary by inserting an extra row of adatoms between two largely unperturbed 7×7 HUCs [62]. They noted that this model increased the density of dangling bonds by \(\sim 10\%\) over 7×7.
The landmark paper by Itoh et al. specifically outlined the rationale behind the models presented [83]. In addition to the obvious concerns of adatom agreement with STM and dangling bond reduction, they specifically list the moieties taken from the DAS reconstruction that they consider as building blocks. The valid components are:

1. adatoms on $T_4$ sites
2. restatoms
3. dimers
4. bonds between dimers and atoms in the stacking fault layer
5. faulted stacking
6. ideal tetrahedral bonding

With these principles, they constructed models for four of the boundaries they observed. In their notation, these were (1,6), (3,5), (5,2), and (3,6). Several common features arise: flipped adatoms, whose placement changes from the normal $2 \times 2$ arrangement to a local $4 \times 2$ spacing. These occur when corner adatoms are displaced inward along the edge of the HUC, and the edge adatom is removed. Dangling bonds on dimers are common. Boundaries have an alternating appearance with a unit cell that is twice the $7a_o$ minimum.

Gu et al. [59, 60] observed and provided structures for five different domain boundaries. Three of the boundaries they examine had period doubled unit cells that alternated between two different configurations. These arose when corner adatoms at the boundary. Like Itoh et al., they were able to explain the atomic structure of all of their domain boundaries using DAS motifs. Further examples of DAS domain
boundary structures, all constructed using more or less the same approach, can be found in Refs. [121, 214, 229, 215, 230]

7.8 Summary

The previous studies of domain boundaries on reconstructed surfaces have been reviewed. Since the focus here will be boundaries between domains of 5×5, particular emphasis was placed on 7×7 boundaries, the closest reconstruction for which there exists a body of literature. The important points are that for DAS reconstructions domain boundaries are restricted to be phase boundaries (tilt and twin boundaries are excluded), and there is a practical labeling scheme which, for uniform boundaries, gives uniquely identifies the atomic structure of the boundary. Finally, on 7×7, all instances of uniform boundaries have been found to propagate parallel to the short diagonals of the unit cell.
Chapter 8

Domain Boundary Notation

This short chapter serves to introduce a new notation for describing DAS domain boundaries. The overall goal of the notation is to unambiguously identify the local atomic environment of a boundary. This notation will be called standard representation. It labels the boundary’s character.

First the different factors which distinguish one boundary from another will be established. This will lead to a simple shift vector notation which describes the relative shift between two domains and the direction of propagation of the boundary in terms of an absolute basis. The basic principles of standard representation will be identified and its use illustrated. The scheme is based on the notation introduced by Itoh [83], but more precisely defines the manner in which it can be applied, introduces some notational adjustments, and expands the scheme to allow the description of domain boundaries which traverse other directions. Finally we will briefly discuss the symmetry of DAS domain boundaries, and identify their chirality. This chapter is meant to provide an introduction to the notation before the atlas of observed boundaries is presented in Ch. 9. A more thorough exploration of the notation is
8.1 Shift Vector Notation

8.1.1 The Unit Vectors

As discussed in Sec. 3.5, all DAS reconstructions have $p3m1$ wallpaper group symmetry. For this section, rather than drawing the atoms of the unit cell, we will use as a schematic the regular tessellation shown in Fig. 8.1 which has the same wallpaper group. The dark triangle represents the unfaulted half of the unit cell. The unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are always chosen so that they straddle either side of the UHUC, and form a right handed set with $\mathbf{a}_3 = \hat{z}$. Appendix B presents some useful mathematical tools for working in a hexagonal basis. Clearly this choice of alignment is not unique. There are three different orientations, separated by $120^\circ$, that are valid axes possibilities. One effect of this degeneracy is that equivalency of domains can be obscure. Standard representation in intended to overcome this problem.
8.1.2  The Shift Vector

The first, and most fundamental, characteristic of a domain boundary is the relative shift between the two domains. This is a vector $S$, expressed in the basis of the lattice vectors $a_1$ and $a_2$. It is well defined for any boundary between equivalent irrotational domains, regardless of the degree of order of the boundary itself. For a shift between domain 1 to domain 2 of $S_{12}$ the reverse, from domain 2 to domain 1 is given by $S_{21} = -S_{12}$. The sum of the shift vectors around any closed loop will always equal zero

$$\sum_i S_i = 0, \quad (8.1)$$

so long as the loop does not contain any bulk dislocations, and all the $S$ use the same basis.

Since domains are built upon the same substrate only discrete shift vectors are possible, and for DAS the orientation of the unit cell is fixed from one domain to the next. So for the $N \times N$ DAS reconstruction $S = \frac{n}{N}a_1 + \frac{m}{N}a_2$ where $n$ and $m$ are the integer shift indices. As a short hand we write $S = [n \ m]$, and we will adopt the crystallographer’s convention of indicating negative indices with an overbar. Since the shift of an entire unit cell $S = [N \ N]$ is clearly no shift at all, the indices of $S$ will always be presented in symmetric modulo form ranging from $-(N-1)/2$ to $(N-1)/2$ (see Appendix B for details on the symmetric modulo). For an $N \times N$ reconstruction there are $N^2 - 1$ possible shifts between two domains (the -1 accounts for the trivial non-shift $[0 \ 0]$). So for $5\times5$ there are 24 different shifts.

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1The shift vector we use here is based on, but differs slightly from the one introduced by Itoh et al. [83]. First our basis vectors are selected so they straddle the UHUC, rather than FHUC. Secondly, as explained in the next paragraph, our indices are reduced using the symmetric modulus rather than the conventional one.
The possible shifts between two domains can be expressed graphically with a shift rose, illustrated for 5×5 in Figure 8.2. Each node of the rose indicates an allowed shift. Some nodes are redundant, retained to maintain the symmetric appearance (e.g. [2 2] for instance shows up twice).

### 8.1.3 The Translation Vector

The second parameter of interest, and the one that is generally easiest to identify, is the direction of propagation of the boundary. Experimentally only two directions are observed: we call those boundaries that run along the short diagonal of the unit cell (i.e. along the (11) family of directions) A-type and those along the long diagonal of the unit cell ((11) directions) B-type.

A well-ordered boundary can be divided into straight uniform segments and a unit cell, local to the boundary, defined for each segment. The translation vector
expresses the direction and distance that the unit cell must be tiled to build the segment. The translation vectors for the two boundary types are $T_A = \langle 1\bar{1} \rangle$ and $T_B = \langle 11 \rangle$, where $\langle \rangle$ indicates the family of direction of the same form. Registration with the surrounding normally ordered domains insists that the translation vector be an integer multiple of $T_A$ or $T_B$.

### 8.1.4 Shift Vector Notation

At its simplest, shift vector notation describes a domain boundary in terms of its shift and direction of propagation using a consistent basis. So, for instance, a boundary might be described as having shift $S_{12} = \[2 \bar{2}\]$ with propagation direction $T = [1 0]$. Other boundaries can be described in the same manner, and Eqn. 8.1 can be used to relate them to one another. This is very straightforward, useful, and is often all that is needed, but the next section will illustrate the benefits of enforcing a standard representation scheme.

### 8.2 Standard Representation

Consider two domains with shift vector $S_{12} = [n \ m]$ separated by a boundary which propagates along $T_1 = T_A$. If, instead, the boundary is viewed from domain 2, rather than domain 1 then the shift vector is $S_{21} = [\bar{n} \ \bar{m}]$ and the translation vector $T_2 = -T_A$. Clearly, these are the same boundary, but the notation does not make that obvious. Are they the same as another boundary with the same shift, $S_{34} = [n \ m]$ but different translation vector $T_2 = [\bar{r} \ \bar{s}]$? In general, no.

For any given boundary, the shift vector origin can be placed on either of the
The six possible ways to denote a single boundary using shift notation. In standard representation there is only one label, A[2 1].

Figure 8.3: Shift Notation vs. Standard Representation.
two domains, where it can point along any of the three different directions that have \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) straddling the UHUC. Moving the origin from one domain to the other inverts \( \mathbf{S} \) which is equivalent to a \( 180^\circ \) rotation. Each of the three direction choices corresponds to a \( 120^\circ \) rotation of \( \mathbf{S} \). So combinations of relocating the origin and selecting alternate axes orientations result in six different choices of shift vectors, separated at intervals of \( 60^\circ \), that could apply to this one domain boundary!

Standard representation is a scheme that permits only one label for any boundary. It allows identification of equivalent boundaries independent of propagation direction, and choice of basis orientation. A domain boundary index is in standard representation if;

1. \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) straddle the UHUC. In terms of the 3D crystallographic directions, this means that \( \mathbf{a}_1 + \mathbf{a}_2 \) points along \([\bar{1}\bar{1}2]\), \([2\bar{1}\bar{1}]\), or \([\bar{1}2\bar{1}]\).

2. The coordinate system is oriented so that, in terms of the basis chosen in step 1, \( \mathbf{T}_A = [1 \bar{1}1] \) for A-type boundaries, and \( \mathbf{T}_B = [1 11] \) for B-type boundaries.

3. The reference domain is selected so that, when viewed from the reference domain, \( \mathbf{T} \) points to the right.

The indices of domain boundaries with axes defined using the above procedure are unique to that boundary. So, under this scheme there is only one way to identify the boundary in Fig. 8.3. When in standard representation the indices combined with the boundary type are referred to as the boundary’s label and will be written as \( A[n \, m] \) or \( B[n \, m] \) for A-type and B-type boundaries. So the boundary in Fig. 8.3 is \( A[2 \, \bar{1}] \). The symbol \( \Lambda \) will be used for labels in standard representation, and \( S \) will be reserved for indices which may or may not adhere to the restrictions of standard
representation.

This scheme does have drawbacks. Because the coordinate orientation is rotated to adhere to the rules above, the indices are not referenced to an absolute and universal basis. So, for instance, summing the labels around a closed loop does not give zero, like it would for shift vectors. More details of performing arithmetic on labels with application to common features will follow in Ch. 10.

On the other hand, the boundary’s label reflects, or at least identifies, the local atomic environment in the vicinity of the domain boundary. Itoh’s insight was that the structure of the boundary itself is defined by that local environment [83]. Thus the boundary’s label, by identifying the local conditions, also specifies the atomic structure. So in the same way that specifying a surface’s Miller indices identifies the atomic structure, the label will similarly identify the boundary. One of the goals of Ch. 9 is to assess how well this postulate is supported by the experimental evidence.

8.3 DAS DB Symmetry

8.3.1 1D Symmetry

In 1D there are only 2 isometries: translation along one dimension and reflection in a point along the line. Thus, the only point group symmetries are the identity and reflection, and two corresponding point groups: one that contains the identity and reflection, and another which contains only the identity. Similarly, there is only one 1D lattice: an array of evenly spaced points. The combination of one lattice and two point groups means that there are only two 1D space groups: one with reflection symmetry about two distinct points in the unit cell, and one which possesses only
8.3.2 2D Strip Symmetry

There is a class of objects intermediate between the infinite 2D plane and the 1D line, these are 2D semi-infinite strips, sometimes called friezes, which have finite width, but stretch infinitely along the dimensions perpendicular to their width. Only those 2D isometries which do not shift the strip outside of itself are candidates for symmetry operations. So the list of valid isometries for a frieze is reduced to:

- Identity

- Translations by $T$

- Reflection in any axis perpendicular to $T$

- Reflection in the longitudinal axis of the strip

- Glide reflection in the longitudinal axis of the strip

- Rotation by $180^\circ$

Every frieze possesses the first two symmetries — the first trivially, the second by the definition of a frieze. These will be found in combination with the remaining symmetries as a frieze group; the 1D analogue to the 2D wallpaper groups and 3D space groups. There are seven frieze groups whose cell diagrams are shown in Fig. 8.4. Figure 8.5 summarizes the symmetries of each of the seven frieze groups.
Figure 8.4: Examples of and cell diagrams for the seven frieze groups. The symbology follows that introduced in Sec. 3.5.

Figure 8.5: Frieze Group Symmetries. The columns indicate the three possible symmetries: rotation by 180° about a point in the line (R), reflection in an axis perpendicular to the line (⊥), reflection in the line (∥) and glide reflection in the line (G).
8.3.3 The Repeat Vector

Aside from the label, which includes information on the domain shift and boundary propagation direction, another piece of information is required to assess the boundary’s symmetry group. This is the repeat vector. Care should be taken to distinguish the between this vector denoted $\mathbf{R}$ and the rotation operation $\mathbf{R}(\theta)$. The difference should be clear, not only from context, but by the fact that rotation will always include an angle argument.

If the shift and translation vectors are thought of as defining a boundary’s boundary conditions, then the repeat vector describes the atomic arrangement adopted by the boundary. It is defined as the shortest vector that will displace a unit cell from the normally ordered region in one domain into congruence with a normally ordered cell in the second domain. Thus it is a measure of the width of anomalously ordered region at the boundary.

\[
\mathbf{R} = \mathbf{S} + p\mathbf{a}_1 + q\mathbf{a}_2 \quad (8.2)
\]
\[
= \mathbf{S} + [pq]. \quad (8.3)
\]

Observationally, for A-type domains $p = q = 0$, or $p = 1$ and $q = 0$. Large values of $\mathbf{R}$ correspond to wide domains, which are not generally seen. For B-type domains, $p = 0$ and $q = 0$.

8.3.4 Conditions for Symmetry

Since the DAS has $p3m1$ symmetry, it contains only 3-fold rotations and, since $C_2$ is not a subgroup of $C_3$, a DAS domain boundary cannot possess frieze rotation
symmetry. So the domain boundaries must be either F1, F2, F3, or F4. This restricts the task to identifying the presence or absence of parallel, perpendicular, and glide reflection symmetry in the boundary.

The rules that guide this search are;

**Reflection** \( \parallel T \) Reflection axis parallel to \( T \) and perpendicular to \( R \).

**Reflection** \( \perp T \) Reflection axis perpendicular to \( T \) and the projection of \( S \) onto \( T \) translates one perpendicular reflection axis into another.

**Glide Reflection** Reflection or glide axis parallel to \( T \) and the projection of \( R \) onto \( T \) is \( \frac{1}{2} T \).

### 8.3.5 A-type Boundaries

**\( \perp \) Reflection**

There is only a \( \perp \) reflection axis. Only \( S \) parallel to [11] will have \( \perp \) reflection symmetry. So, shifts having \( n = m \) will possess \( \perp \) reflection symmetry, all others will not.

**\( \parallel \) Reflection**

There is no reflection axis \( \parallel \) to \( T \), so there can be no \( \parallel \) reflection axis, regardless of \( S \) or \( R \).

**Glide Reflection**

Again, there are no reflection or glide reflection axes parallel to \( T \), so there is no glide reflection symmetry, independent of \( S \) or \( R \).
A-type Frieze Assignment

The forgoing analysis demonstrates that there are no parallel or glide reflection symmetries possible for A-type boundaries. But, if \( n = m \) there will be \( \perp \) reflection symmetry, which places the boundary in F4. All other boundaries fall into the only remaining possibility, namely F1. This is summarized by the shading of the rose in Fig. 8.6

8.3.6 B-type Boundaries

\( \perp \) Reflection

There are no reflection axes in the unit cell that are perpendicular to \( T \).

\( || \) Reflection

There are reflection axes parallel to \( T \) so the first condition is met. Are they perpendicular to \( R \)? This can be checked by verifying that \( R \) is perpendicular to \( T \), since
CHAPTER 8. DOMAIN BOUNDARY NOTATION

\( \mathbf{T} \) is parallel to the reflection axes;

\[ \mathbf{R} \perp \mathbf{T} \Rightarrow \mathbf{R} \cdot \mathbf{T} = 0 \quad (8.4) \]

\[ \mathbf{R} \cdot \mathbf{T} = \frac{1}{N}(\alpha n + \beta m) + \alpha p + \beta q \quad (8.5) \]

where \( \alpha = s + \frac{1}{2}t \) and \( \beta = t + \frac{1}{2}s \). For B-type boundaries \( \alpha = \beta = \frac{3}{2} \). So

\[ \mathbf{R} \perp \mathbf{T} = n + m + p + q = 0 \quad (8.6) \]

Since \( p \) and \( q \) are integers, \( \frac{n+m}{N} \) must be an integer too. But in the restricted range of \( n, m \) the only possibility is \( n + m = 0 \). So

\[ n + m = p + q = 0. \quad (8.7) \]

**Glide Reflection**

As above, there are reflection axes. The second condition insists that

\[ 2\mathbf{R} \cdot \mathbf{T} = \mathbf{T} \cdot \mathbf{T}. \quad (8.8) \]

The left side was found above, the right side is given by

\[ \mathbf{T} \cdot \mathbf{T} = t_1^2 + t_2^2 + t_1t_2, \quad (8.9) \]

\[ 2\mathbf{R} \cdot \mathbf{T} = \mathbf{T} \cdot \mathbf{T} \Rightarrow \frac{n + m}{N} + p + 1 = 1. \quad (8.10) \]

So the condition for glide is that \( n + m = 0 \) and \( p + q = 1 \).
B-type Frieze Assignment

For B-type boundaries only shifts where \( m = \bar{n} \) can have higher symmetries. All other boundaries will fall into F1. If \( m = \bar{n} \) then the frieze group assignment will depend on \( R \), i.e. the details of the atomic arrangement at the boundary. If \( p + q = 0 \) then there will be parallel reflection, if \( p + q = 1 \) there will be glide, and otherwise there will be neither. In the first case the boundary has symmetry F3. In the second it has F2, and in the third F1. This is summarized in Fig. 8.6.

So, DAS domain boundaries can possess any of the four frieze symmetries available to them, depending on the arrangement of \( S \), \( T \), and \( R \).

8.3.7 DB Chirality

The chirality is a useful quality with which to classify boundaries. The boundaries with F2, F3, and F4 symmetry possess a reflection symmetry. These achiral boundaries are those having labels \( A[n \bar{n}] \) and \( B[n \bar{n}] \) (with appropriate \( R \)). On the other hand, those that fall into F1 are chiral. For A-type boundaries, the chiral enantiomorph of \( A[n m] \) is \( A[m n] \). For B-type boundaries, the pairs are \( B[n m] \) and \( B[\bar{m} \bar{n}] \).

8.4 Summary

This chapter introduces a notation for describing domain boundaries based on that of Itoh, but expanded to include B-type boundaries. Consideration of DAS domain boundaries as friezes show that they can have the symmetries of four of the seven possible frieze groups, depending on the boundary’s misfit, direction of propagation,
and width. The next chapter catalogs the experimental observations of such domain boundaries.
Chapter 9

Atlas of Ge $5\times 5$ Domain Boundaries

This chapter presents observations of domain boundaries seen on the Si(111)-Ge($5\times 5$) surfaces. The focus here is on the atomic structure of each of the observed boundaries. The chapter begins by describing the surface preparation procedure, and the techniques for identifying the character of domain boundaries. A description is presented of the rational behind the atomic models for each boundary, accompanied by a summary of important statistics for each. Finally, the bulk of the chapter is devoted to a comprehensive catalog of all the observed domain boundaries.

9.1 DB Surface Growth Procedure

The preparation procedure began with the creation of Si(111) $7\times 7$ according to the procedure outlined in Sec. 3.9. The Ge overlayer was prepared using the solid phase epitaxy technique described in Sec. 5.5. First, 1 or 2 BL of Ge, as measured by
the thickness monitor, was deposited onto a cold substrate to produce an amorphous structure. Annealing at 480–510° C for 15-30 min generated order. The long anneal promotes uniformity of the domains and their boundaries. A selection of results of this procedure can be seen in Fig. 9.1. Figure 9.1a shows a surface annealed at 480° C with 1.85 BL of Ge, measured by flooding analysis. The target coverage was 2.0 BL. Incomplete coverage is due to irregularity of the evaporator rate. The holes, areas where the second bilayer is incomplete, have an average diameter of \( \sim 25 \text{ nm} \). Their large number is an indication of the success of the SPE process at encouraging domain nucleation even though the scale of Fig. 9.1a renders individual domains invisible. Near the step edge, where a preexisting nucleation feature is present, there are no holes. Closer views, shown in Fig. 9.1b and c show a network of domain boundaries, marked by the perforation-like striations, running between the holes and connecting between themselves at vertices. Figure 9.1d shows a large scale image of a surface where the terrace width is smaller, the coverage was complete, and the annealing temperature, 510° C, was slightly higher. Here there are no holes, but the terraces are covered with a network of domain boundaries, seen up close in Fig. 9.1e.

The domain boundaries seen in Fig. 9.1 show a variety of different types, but they share some common characteristics. First, locating them is made easy by the dark holes that form part of their structure. We call these boundary holes and they form when the corner holes of adjacent domains combine. As foreshadowed in the previous chapter, when the A-type and B-type boundaries were introduced, the propagation direction of the boundaries does fall along either the short or long diagonal of the unit cell. Some of the boundaries are very straight, and express few defects. Others are composed of several segments of different types separated by kinks. In all cases
Figure 9.1: 5×5 Domain Boundaries. a) ~1.85 BL of Ge. Pockets of incomplete coverage in the second bilayer are visible as dark triangles. Domain boundaries connect the pockets as shown in b. b) Domain boundaries between the voids. The dark boundary holes clearly delineate the boundary between adjacent domains. c) Closeup of the indicated section of b. d) Another surface with 1 BL of Ge. e) Closeup of d) showing more domain boundaries.
Figure 9.2: Explicit Indexing. Hexagonal grids are applied to both domains, registered with the pronounced corner holes. The shift rose is oriented according to the constraints of Sec. 8.2 so that the left domain is the reference. The boundary is revealed to be A[22].

though, the boundary threads its way between its start and finish vertices along a path with no wild excursions. It will be seen that the visual appearance of the boundary, which of course is a manifestation of its atomic structure, uniquely identifies its label. This means that the following catalog can be used to identify boundaries based on their appearance.

9.2 Indexing Domain Boundaries

Two techniques were used to determine the indices of domain boundaries from an STM image. When the image is of good quality the boundary shift and propagation direction can be measured directly: this is explicit indexing. On the other hand, if image quality is low, then the label can only be identified implicitly, based on the identity of adjacent boundaries and topological considerations. Explicit indexing is
Figure 9.3: Implicit Indexing. Three domains and their associated boundaries meet at a common vertex. The indices of any boundary can be deduced if the other two are known. In this case $\Lambda_{12}$ and $\Lambda_{23}$ can be recognized as $A[11]$ and $B[22]$ boundaries respectively. The arrows indicate the conventional direction of $T$ for each boundary.

shown in Fig. 9.2. From other images the UHUC is known to point to the left, as shown by the diamond unit cell. The shift rose is aligned according to the rules presented in Sec. 8.2 ([10], and [01] straddle the UHUC, origin domain chosen so that $T = 1\bar{1}]$ points to the right). Then it is simple a matter of directly reading the shift from the rose — this is an $A[22]$ boundary. Implicit indexing of a domain boundary, useful when image quality is poor, relies on knowing the shifts for boundaries nearby. By taking advantage of Eqn. 8.1, which states that the sum of the shift vectors around a loop must equal zero, the unknown shift can be determined. The shifts for the known boundaries can be found from explicit indexing, or through recognizing boundaries from their known appearance. Boundaries $A[11]$ and $B[22]$, in particular, are plentiful and distinctive enough to be recognizable even in marginal images.

Figure 9.3 shows three intersecting boundaries. In this particular case, the image
quality is excellent, so explicit imaging is possible and preferable, but it serves as a
good example of using implicit indexing to find $A_{31}$. $A_{12}$ and $A_{23}$ are easily recognized
as $A[11]$ and $B[22]$. When expressed as shifts in terms of the common basis shown
by the rose, these are $S_{12} = [2\ 1]$ and $S_{23} = [2\ 2]$. Completing the loop requires that
$S_{31} = [0\ 1]$, which has label $A[01]$. The loop can be extended to include as many
boundaries as necessary, and multiple loops can be used together to identify several
unknown boundaries, so long as the number of unknowns does not exceed the number
of loops. Further details of implicit indexing will be presented in the next chapter on
vertices.

9.3 Domain Boundary Catalog

This chapter presents a comprehensive catalog of observed regular domain boundaries.
Examples are presented for all of the 14 A-type boundaries, and three of the possible
B-type. Two of the A-type boundaries were only observed in one enantiomorphic
form ($A[\bar{1}\ 2]$ and $A[0\ \bar{1}]$). Some boundary types are more common than others. When
possible, the most illustrative images are presented. In other cases when only one
specimen is available, it is presented in spite of its faults.

Some boundary types are more prone to disorder than others, and they express
variants having different AO unit cells. Generally though, one variant dominates
and, in most cases, the principle that a boundary’s label reflects a unique atomic
configuration is found to be true. So, for instance, the label $B[\bar{3}\ 2]$ not only describes
the shift between two domains and the direction of boundary propagation, but it is
a useful and unambiguous identifier of a unique atomic structure. It is also observed
that, for most of the chiral boundaries with both enantiomorphs observed, that the
mirror forms are predicted by the rules established in Sec. 8.3.7. That is, the atomic structures of A[\(n m\)] and A[\(m n\)] are indeed mirror forms, as are B[\(n m\)] and B[\(\bar{m} \bar{n}\)]. The notable exception is A[\(1 2\)]/A[\(2 1\)] for which only very small samples are available.

For each boundary type an STM image is presented. When appropriate, smoothing and distortion correction were applied to ease interpretation. For chiral boundaries, both enantiomorphs are shown if available. Generally, the images are empty state ones, but when possible, filled state images are included too. A stylized version of the images are presented as a schematic free of imaging artifacts. A model is also proposed for each of the boundaries. In cases where the boundary has common variants, models are presented for each. For ease of interpretation, the image, schematic and model, are oriented in a consistent fashion as in Fig 8.6. For A-type boundaries that means that the boundary runs vertically and for it runs B-type horizontally. In both cases \(\mathbf{a}_1 + \mathbf{a}_2\) points to the right.

The unit cell for each boundary defines the limits of the anomalously ordered region between the two adjacent domains. When a boundary expresses, variants they are distinguished with dashed or dotted unit cells. They are drawn along the natural boundaries defined by the dimer rows and corner holes of the adjacent normally ordered cells. In general, the unit cell has been drawn so that it is as small as possible. However, if variants have different sizes, a consistent and, if necessary, non-minimal unit cell is used to allow direct comparison between them. Table 9.1 shows the unit cell area, and the number of dangling bonds contained in each of the domain boundaries.
Table 9.1: Domain Boundary Summary. For each boundary type, the table lists the unit cell area (in units of 1×1), the number of dangling bonds, and the dangling bond density (dangling bonds per 1×1 unit cell). For boundaries with common variants, the values for both structures are presented. The values for 5×5 and 7×7 are included for reference.
Models

For all of the observed boundaries a model was developed based on considerations similar to those presented in [83, 230, 59], albeit with some modifications. Each is constructed from simple building blocks, assembled so as to match the observed images and minimize the total number of dangling bonds. In general, the observations are consistent with the lowest dangling bond density model allowed by the building blocks.

The first principle was the assumption that the bright protrusions visible in empty state images are adatoms. The locations of adatoms in the model must match the locations of bumps in the images. Without more complex calculations, the best available measure of a model’s energy is the number of bonds it leaves unsaturated. Thus, models with fewer dangling bonds are preferred to ones with more dangling bonds. Since double dangling bonds are very expensive, they are forbidden; all atoms must be at least three-fold coordinated. To crudely account for the effects of strain, structural motifs are restricted to those taken from the DAS structure, which are demonstrably energy efficient. Dangling bond density is necessarily increased at a domain boundary. New motifs are introduced by breaking bonds on the only atoms that are fully coordinated, and for which an added dangling bond will not defy the proscription on double dangling bonds. This generates three new types of atoms: dangling dimer atoms, dangling dimer layer atoms and dangling restlayer atoms. These are shown in Fig. 9.4.

The number of dangling bonds for each model is summarized in Table 9.1.
Figure 9.4: Model Building Blocks. a) The standard DAS moieties. b) Two new motifs: a dimer layer atom with a dangling bond, and a restlayer atom with a dangling bond. c) The two new motifs that come from adding one and two dangling bonds to a dimer.
9.4 Achiral A-Type Boundaries

9.4.1 A[1 1]

Empty state STM images like Fig. 9.5a show five bright adatoms within each DB unit cell with enlarged corner holes separating the cells. It appears that the two domains of $5 \times 5$ are cleanly truncated and a row of extra adatoms have been interposed between the adatoms from each half.

Figure 9.5e shows the proposed model of the domain boundary. Inserted between the halves of a largely unmodified $5 \times 5$ unit cell are two extra adatoms each with three supporting restlayer atoms below. The dimer remains attached to one half of the unit cell and shifts off the cell centreline to accommodate the new adatoms. In this example, the adatoms are accommodated in the UHUC and the dimer line shifts towards the FHUC. The extra adatoms form the usual rectangular pattern with adatoms across the dimer line. However, they also form the same pattern with the dimers on the same side of the dimer line. This leads to the unusual “six-pack” appearance of the boundary.

This unit cell has an area of 22.5 (in terms of $1 \times 1$ unit cells). There are now 5 adatoms dangling bonds, and 2 restatoms. The enlarged corner hole contains $5 \frac{1}{2}$ atoms with dangling bonds; 2 from the restlayer layer, 2 from the dimer layer and $1 \frac{1}{2}$ from the bulk layer. That is a total of $12 \frac{1}{2}$ dangling bonds, or 0.56 dangling bonds per $1 \times 1$ unit cell, compared with 0.36/1×1 for $5 \times 5$.

Such a high density of dangling bonds in the corner hole is almost certainly relieved by the addition of more atoms. However, because of the geometry, none of the DAS moieties are compatible. STM images are of little help aside from showing that the
Figure 9.5: $A[11]$. a and b) Empty state STM image at +1.74 V and schematic of the same area. c) Filled state STM image at -1.52 V and corresponding schematic. The arrows indicate which side of the boundary the extra restatom lies in, and thus which HUC has been extended: for arrows on the left the UHUC is the larger, for arrows on the right it is the FHUC. d) Proposed structure for $A[11]$. 
hole is deep and elongated. This can rule out protruding structures (i.e., the hole must be a hole). The details of the corner hole geometry will require atomic level modeling with DFT.

The structure shown in Fig. 9.5 shows the extra adatoms extending the UHUC. An analogous structure comes from leaving the dimer line attached to the UHUC, and adding the adatoms to the FHUC instead. In both cases the adatoms lie exactly midway between the halves, but in the latter case the extra restatom is in the faulted, rather than unfaulted HUC. Effectively the two options are to have a large UHUC or large FHUC. Since the UHUC is energy favoured versus the FHUC the former case is expected [149, 151]. In the filled state image of Fig 9.5, away from the boundary, diffuse protrusions are visible between the three adatoms of a HUC. On the other hand, dimer rows are clearly dark. The protrusions are interpreted as restatoms, visible owing to a fortuitous tip configuration, which contrast with the dark gap found over dimers. Examining the domain boundary itself the extra restatoms, highlighted with arrows, are again visible. The opposite side of the rectangle has a dark gap, like that associated with dimer rows. The presence of a dimer row on one side of the extra adatoms, and an extra adatom on the opposite side, supplies strong support to the model in Fig. 9.5. Perhaps most interestingly, the alignment of extra restatoms alternates between FHUC to UHUC along the length of the boundary. This is a small specimen, but it suggests that the preferred boundary unit cell is actually a pairing of that shown in Fig. 9.5 with the analogue that comes from inserting the extra adatoms into the FHUC rather than UHUC. In the language of Sec. 3.5 this means that $\mathbf{T} \neq [1\bar{1}]$ but it is instead $[2\bar{2}]$. 
9.4.2 A[2 2]

Figure 9.6a and 9.7 show STM images of a rare A[2 2] boundary. It is unusual in that the translational periodicity is twice $T_A$. For simplicity, the AO unit cell is divided into two parts. Part I, drawn with solid lines, and II with dashed lines. They point in opposite directions, but have equal areas. Together they make the complete unit cell. The appearance of A[2 2] is of the letter “g” and its mirror image paired back to back. The parallel spines of the “g”s form a huge rectangular block four adatoms wide by two high. The 3 o’clock atoms in the corner hole ring make equilateral triangles with the two central atoms in each spine, but the spacing between the atoms is $\sqrt{3}a$ rather than the usual 2a spacing between adatoms in a HUC of 5×5. The tails of the “g”s enclose elongated corner holes. Between the tails lies a fuzzy protrusion that is ascribed to an adatom, although in Fig. 9.6 its intensity is lower than the adatoms that surround it. In Fig. 9.7 it has the same intensity as the others. This adatom and the four others around it form a local 2×2 reconstruction.

Figure 9.6c shows a proposed model of A[2 2]. In section I the stacking is entirely unfaulted, in section II it is faulted (aside from the small intrusion at the top and bottom). The left three adatoms of section I (solid lines) are in the conventional 5×5 HUC arrangement. The four adatoms to the right of the section are in a pattern described in matrix notation by

$$\begin{pmatrix} 1 & -2 \\ 1 & 2 \end{pmatrix}$$

The two rightmost adatoms bridge with dimers to the opposite FHUC in the conventional way. However, they both have one restlayer atoms unsaturated. The adatoms that lie at the top and bottom of section I has a $\sqrt{3}$ arrangement with the three nearest adatoms of section I. The corner hole ring at the left of the boundary does not have the usual atomic geometry.
Figure 9.6: A[22]. a) STM image of A[2 2] (V = 1.5 V). b) Schematic of panel a. The boundary unit cell is twice the shortest translation distance. For convenience, it has been divided into two sections labelled I (solid lines) and II (dashed). c) Proposed atomic structure of A[2 2].
of alternating adatoms and dimers. Instead, between 2 and 8 o’clock, it is formed from a small section of $\sqrt{3}$. The 3 o’clock adatom is bonded to section II through a dimer, and to the right bonds to a dimer, that being adjacent to the boundary hole, has two unsaturated bonds. Of these dimer dangling bonds, the ones within section I of the unit cell are very close to the dangling bond carried by the restlayer atoms supporting the rightmost adatoms. Since a bond between these two is not allowed in our set of components we have not drawn it in. However, some overlap between the dimer and restlayer atom dangling bonds is certainly possible.

Section 2 consists of 6 adatoms arranged in a $2 \times 2$ fashion, like a $9 \times 9$ DAS FHUC with two missing corner and edge adatoms. The central adatom is surrounded by three restatoms. This unique local environment may account for the contrast difference between it and its neighbours, like that seen for the interior adatom in Si(111)$9 \times 9$ [18]. Both of the two right restatoms are supported by two unsaturated dimer layer atoms.
The period doubling of this boundary remains puzzling. The key point is that either section I or section II make perfectly valid and repeatable unit cells on their own. Why are both sections present and why are they paired, even in the face of disorder inducing kinks, as shown in Fig. 9.7? The easiest explanation is that the model presented in Fig. 9.6c is simply wrong, and that the true unit cell cannot be divided into subunits that can stand on their own as independent unit cells. Unfortunately, the symmetry of the adatom positions reflects the fact that the symmetric boundary conditions which define the two sections demand that they be independently repeatable subunits, even if the structures presented here are not correct in the details. What can be said about the energy of the two sections? In total there are 20 $\frac{1}{3}$ dangling bonds in section I, and 18 $\frac{1}{3}$ in section II. So on the basis of counting dangling bonds, it seems that section II should be clearly preferred, and more frequent, which is not the case. Furthermore, that the sections pair so consistently (every time in an admittedly small sample) indicates that this is not a manifestation of the disorder seen in some of the other boundaries. So pairing must somehow lead to energy minimization. How? The prime suspect is that the two sections generate strains of opposite sense. If tiled independently, the strain would accumulate quickly. But when paired, the strain of one section relaxes the strain from the other, reducing the cumulative boundary energy.

9.4.3 $\mathbf{A[\bar{2} \bar{2}]}$

STM images of $\mathbf{A[\bar{2} \bar{2}]}$ are shown in Fig. 9.8a and b. Both images are taken over the same area, the former at $+0.95V$ and the latter at $+1.81V$. The most visually distinctive features are the paired corner hole rings on either side of the boundary which
Figure 9.8: $A[\overline{2} \overline{2}]$. a) STM image at +0.98V. b) STM image of the same area at +1.8V. The arrows indicate the unit cells where adjacent corner hole rings on the left side are joined together. c) Schematic of panel b. d) Proposed structure for $A[\overline{2} \overline{2}]$. 
create a spectacle-like appearance. The spectacles are separated by long symmetric corner holes. In general, adjacent corner hole rings are distinct from one another. However some of the corner holes, marked with arrows, have blurry features that join one ring to the next and protrude into the boundary hole. The blur is always found on the left side of the boundary.

Within the domains, the low bias image in Fig. 9.8a shows a slight, but clear, contrast difference between faulted and unfaulted half unit cells, with the UHUC pointing to the left. At the boundary, the adatoms along the side of the boundary hole also show contrast differences with the two on the left brighter than the two on the right. This is taken as an indication that the adatoms on the left are faulted. This is consistent with the location of the joining protrusions indicated with arrows in Fig. 9.8b if they are taken as adsorbed impurities. On the other hand there is no clear contrast difference between the two adatoms at the ends of the holes which bridge the boundary.

The model proposed in Fig. 9.8d has mirror symmetry for the selvedge layers in axes both parallel and perpendicular to the boundary propagation direction. Considering also the substrate leaves only the reflection symmetry perpendicular to the boundary. This model has frieze group F4 symmetry. It consists of two truncated HUC of $5 \times 5$ whose corner adatoms have been removed to create the boundary hole. The truncation leaves behind two exposed dimer layer atoms on either side of the boundary, each with a dangling bond. The two adatoms which bridge the boundary, shown at the top and bottom of the AO unit cell, form a unit cell of $3 \times 3$. The four adatoms at the top of the unit cell form a conventional corner hole ring, and the four adatoms at the bottom do the same. The hole is stretched by interposing a restatom
Figure 9.9: A variant of A[2 2]. a) STM image at +1.41V showing two types of A[2 2] unit cells. The dashed boxes show an extra adatom at the centre of the boundary hole. The solid box shows a similar unit cell to that seen in Fig. 9.8. b) A structure for the dashed unit cell presented in a.

between two of the adatoms on either side. This leaves three bulk dangling bonds at the bottom of the hole.

A[2 2] is a common boundary which most often appears as shown in Fig. 9.8, with large empty boundary holes. Less common is the variant enclosed by the dashed boxes in Fig. 9.9a. In these specimens a distinct protrusion is visible within the boundary hole, precisely centered between the two spectacles. The apparent height of the protrusion is only $\sim 80\%$ that of adatoms within the domains.

No structure composed of DAS moieties, and assembled under the constaints listed in the introduction, can place a single adatom in the centre of the 2× structure in Fig. 9.8d. However, if the faulted restatom is removed, and the truncated UHUC is made
whole, the structure in Fig. 9.9 is formed. In this case, the $5 \times 5$ UHUC on the right penetrates into the truncated FHUC on the left. However, the unfaulted stacking has lower energy and the structure that is shown will, therefore be preferred. Completing the HUC eliminates all dangling bonds on the bulk layer and reduces the number on the dimer layer to one, but it leaves dangling bonds on the two new dimers. This arises because the adjacent faulted and unfaulted adatoms, rather than being directly opposite one another across the dimer, are instead shifted. This dangling dimer bond, and the resulting charge transfer, may be responsible for the darker appearance of the new adatom in the STM images. This structure has a total of 12 dangling bonds, four fewer than the model shown in Fig. 9.8. Given the large reduction in dangling bonds, it is unclear why this model is not the dominant configuration.

9.4.4 $A[\bar{1} \bar{1}]$

Figure 9.10a shows a constant current topograph of the very rare $A[\bar{1} \bar{1}]$ variety. It is characterized by deep, almost triangular-shaped holes whose long axis stretch in the direction of boundary propagation. The adatoms to the left appear to be unperturbed from their normally ordered positions. To the right of the boundary, the three adatoms that ring the half of the corner hole nearest the boundary also appear unchanged. The leftmost adatom in the ring forms a $2 \times 2$ pattern with the three adatoms of the UHUC to the left of the boundary.

Figure 9.10 shows a possible structure for $A[\bar{1} \bar{1}]$. The AO unit cell is divided into two regions. In the centre, there is a FHUC of $3 \times 3$ containing a single adatom. This is flanked by a truncated UHUC of $5 \times 5$ that is missing the leftmost adatom. The unfaulted adatoms of the unperturbed left boundary are shifted relative to the single
Figure 9.10: A[\bar{1}\bar{1}].  a) STM Image of A[\bar{1}\bar{1}], +1.74 V. b) Schematic showing adatom positions. c and d) Structural models, c) based on 3\times3.
faulted $3 \times 3$ adatom. So again, the bonding arrangement on one side of the dimers is shifted from the other. Consequentially the two restlayer atoms which support the $3 \times 3$ adatom are attached to different dimers, which both have one dangling bond. There are two other dangling bonds on dimer layer atoms which support the AO cell’s sole restatom. The total number of dangling bonds is 9.

### 9.5 Chiral A-Type Boundaries

#### 9.5.1 $A[1 0]$ and $A[0 1]$

Figures 9.11a and b show STM images of $A[1 0]$ and $A[0 1]$ boundaries respectively. Focusing on $A[0 1]$ there are two variants visible; the first, drawn with a solid unit cell, dominates. The other, with a dashed unit cell and indicated by arrows, is a slight minority. These are common boundaries and the population of variants is consistent across the many observations that have been made. Variant 1 (solid lines) appears to be an intact FHUC of $5 \times 5$ that has been shifted relative to it’s mate on the other side of the boundary by [0 1]. A deep trench separates the two halves. In variant 2 (dashed lines) the lower two adatoms of the HUC remain unchanged, but the upper adatom shifts by [0 1]. Consequently it is the normal place expected for a $5 \times 5$ adatom.

Models for the two variants of $A[0 1]$ are shown in Fig. 9.11d. Variant 1 (solid lines) is simply the $5 \times 5$ FHUC, complete with surrounding dimers at the perimeter. On the left edge of the HUC, where the shift does not allow matching with the other domain, two rows of dimers attached to opposite domains are left with two dangling bonds each. These unmatched dimers bring a very high density of dangling bonds into close proximity. This may be relieved by more exotic structures disallowed by
Figure 9.11: A[10] and A[01]. a) STM image of A[10] and b) A[01]. c) Schematic of A[01] image. d) Structure of A[01] showing two variants, one with solid unit cell, the other with a dashed unit cell.
the deliberately restricted selection of building blocks.

For variant 2, the top adatom shifts so that it matches the left domain’s dimer. This shifts the pair of unmatched dimers to the other side of the unit cell corner, but it also breaks the lower unmatched dimer for the lower adatom, and exposes a dimer layer atom next to the right adatom. To saturate the exposed dimer layer atoms a restatom is introduced which bonds to one of the exposed dimers from the left domain. These changes affect the distribution of dangling bonds, but not their total: both variants have 13.5 dangling bonds in the unit cells that have been drawn.

Variant 1 (solid cell) is a separation and lateral shift of otherwise unperturbed HUCs. On the other hand, variant 2 (dashed cell) involves reconfiguration of the atoms within one of the HUCs. That rearrangement occurs, almost always, in the FHUC. One of the rare exceptions is indicated by the topmost arrow in Fig. 9.11b where both faulted and unfaulted HUCs have adatoms arranged like variant 2.

9.5.2 A[0 2] and A[2 0]

STM images of A[0 2] and A[2 0] are shown in Fig. 9.12a, b, and c. These are common boundaries and they tend to be highly uniform. Defects are generally limited to kinks like the one seen in 9.12a, and point defects like the one indicated by arrows in 9.12b and c. The filled state images (a and c) show a truncated 7×7 HUC. For A[0 2], the bottom corner adatom is missing. For A[2 0] the top corner adatom is absent. For both boundaries the filled state images have the appearance of a five atom backwards “c” facing towards a matching three atom chevron on the left side. For A[0 2] the chevrons are shifted down relative to the horseshoes; for A[2 0] they are shifted up. The filled state image shows decreased adatom intensity for the five adatoms of the
Figure 9.12: **A[02]** and **A[20]**. a) Empty state (+1.53 V) STM image of A[02]. b) and c) Filled (-1.47 V) and empty (+1.47 V) state images of the same section of A[20]. For registration, the arrows indicate the same defect. The curvature in panel b is an artifact of piezo creep. d) Schematic of the adatoms in panel c. e) Atomic structure of A[20].
truncated $7 \times 7$ suggesting an unfaulted stacking.

The atomic structure for the AO unit cell is shown in Fig. 9.12e. It consists of a truncated $7 \times 7$ UHUC. The cell connects with the three adjacent $5 \times 5$ FHUCs with normal dimer bonds. It attaches to adjacent AO unit cells (i.e. itself) through an extra restatom sitting within the long boundary hole. This restatom is not visible in empty state images, there the hole appears empty. The filled state image show diffuse intensity at the three-fold points between adatoms, and at the location of the connecting restatom. This is consistent with the behaviour of restatoms in filled state images.

This model leaves three unsaturated dimer layer atoms near the boundary hole. There are a total of $12 \frac{2}{3}$ dangling bonds in the core unit cell. Both the enantiomers have unfaulted HUCs of $7 \times 7$. Again, this is because faulted stackings are energetically more costly than unfaulted ones.

9.5.3 $A[0 \bar{2}]$ and $A[\bar{2}0]$

Figure 9.13a and b show STM images of $A[\bar{2}0]$ and $A[0\bar{2}]$. On the left of the boundary, the adatoms appear to be unperturbed and the domain truncates along a vertical dimer line. On the right side there are intact corner hole rings in which the leftmost atom of the ring connects to the half ring of the left domain. This gives the appearance is of a cherry (the corner hole ring) with a stem (the half-ring). For $A[\bar{2}0]$ the stem points up; for $A[0\bar{2}]$ it points down. Within the hook of the stem is a complicated corner hole with no features visible in empty state imaging. This is a very common boundary, but it often contains many kinks, a fact that will be discussed in the next chapter.
Figure 9.13: A[0\bar{2}] and A[\bar{2}0]. a and b) STM Images of A[2\bar{0}], and A[0\bar{2}]. b) Schematic of adatom positions in c. d) Atomic model for A[0\bar{2}].
An atomic model is shown in Fig. 9.13d. Five of the six atoms in the unit cell have unfaulted stacking, consistent with the energy shift for faulted stackings. Three of the adatoms on the left are arranged as a $5\times 5$ unit cell, except that the restlayer atoms which support the top adatom do not connect to a dimer. Instead, they attach to triply-coordinated dimer layer atoms. These support a restatom within the boundary hole and bond to the opposite HUC. The two adatoms of the truncated $5\times 5$ cell on the right side are connected to the boundary hole restatom. A single adatom in faulted stacking configuration forms a HUC of $3\times 3$. It is bounded on all sides by fully saturated dimers, and at the vertices by corner holes. Three dimer layer atoms are left unsaturated. Removing the restatom in the corner hole increases the number of dangling bonds by one and leaves two of the restlayer atoms unsupported. For this model $A[\bar{2}0]$ has a dangling bond density of 0.49 bonds/1×1 UC, the lowest of all $5\times 5$ domain boundaries.

9.5.4 A[0 1] and A[1 0]

Figure 9.14a shows an STM image of $A[\bar{1}0]$. This is a very rare boundary; the short segment presented here, totalling two AO unit cells squeezed between two vertices, is the only observation. The mirror form, $A[0 1]$ has not been observed. There are seven adatoms within the defined unit cell. Six of them can be divided into two three-atom triangles with an unfaulted arrangement. Together, the two triangles form a portion of $9\times 9$ with four missing adatoms. The seventh adatom is the leftmost adatom of the right domain’s corner hole ring. The boundary hole has a complicated zigzag shape, but does not appear as deep as the corner holes in the adjacent domains.

A proposed atomic model for $A[\bar{1}0]$ is shown in 9.14c. The two adatom triangles
Figure 9.14: \( A[0\bar{1}] \) and \( A[\bar{1}0] \). a) Empty state STM image of \( A[\bar{1}0] \). The segment is very short, with only two unit cells, one of which is highlighted, and lies between two vertices. b) Schematic of adatom positions in panel a. c) Atomic structure of \( A[\bar{1}0] \).
do indeed create a large unfaulted fragment of 9×9. The seventh adatom is a FHUC of 3×3 bordered on all three sides by dimers. A row of four restatoms separates the left triangle of adatoms from the 3×3 cell.

9.5.5 A[1 2] and A[2 1]

Figure 9.15a and b show STM images of A[2 1] and A[1 2]. These are very rare boundaries. Both examples include a defect of some sort which may stabilize them. For the A[2 1] example the defect is a large deep vacancy visible at the top of the image, for A[1 2] the boundary connects to a step root just below the bottom of the image. Even between these two small samples there is considerable variation in the atomic arrangement. The rarity of this boundary means that the conclusions drawn here are speculative.

There are two different cores visible in this image, indicated with solid and dashed unit cells. Both variants have three adatoms, but in different configurations. In variant 1 (solid), the lower two adatoms adopt a 2×2 arrangement that, together with the three 5×5 adatoms from the left domain, appears like a truncated 7×7 HUC. The top adatom joins the corner hole ring, which is incomplete missing the top left adatom. For variant 2 (dashed), the bottom adatom remains unmoved, but the upper two adatoms exchange places: the centre adatom moves to the right, and the upper one moves to the left.

Figure 9.15d shows proposed atomic structures for the two variants of A[1 2]. Variant 1 consists of two adatoms of a truncated 5×5 FHUC at the bottom and a single 3×3 UHUC at the top. The truncated 5×5 FHUC is shifted relative to the UHUC to its left so that dimers that connect the two are staggered. One dimer at
the top and a restlayer atom at the bottom are left unsaturated. On the right side of the unit cell the $5 \times 5$ truncation exposes two dimer layer atoms, and two dimers bonded to the UHUC on the right.

In variant 2, the lower pair of adatoms form a unit cell of $3 \times 3$. Again, the dimer to the left is staggered and one dimer atom and one restlayer atom are unsaturated. On the right side the mismatch leaves a restatom and dimer with dangling bonds. Variant 2 increases the number of dangling bonds from 10 for variant 1 to 12.

9.5.6 $A[1 \bar{2}]$ and $A[\bar{2} 1]$

Figure 9.16a and b show STM image of $A[\bar{2} 1]$ and $A[1 \bar{2}]$. The complicated boundary unit cell contains two triangular HUCs pointing in the same direction. For $A[\bar{2} 1]$ the leftmost adatom of the right triangle has a $1 \times 1$ arrangement with the upper adatom of the left triangle. In $A[1 \bar{2}]$ it makes this arrangement with the lower adatom in the left triangle. The corner hole ring of the right domain is intact, but the ring of the left domain contain only four adatoms. A fifth adatom, which is the leftmost adatom of the complete ring, appears to be a member of the left ring, but is actually shifted slightly.

In Fig. 9.16d a model for $A[1 \bar{2}]$ is shown. The two three-adatom triangles both have unfaulted stacking. A single $3 \times 3$ FHUC completes the corner hole ring on the right. This connects to the unfaulted area to the left through a dimer with a dangling bond on one end, and a bond to a restatom at the other. This restatom is one of four that make a long chain. Two are bonded to the dimer that borders the $3 \times 3$ HUC.
Figure 9.17: A[1 1] and A[1 1]. a and b) Empty state images of A[1 1] and A[1 1]. Three variants are visible in b marked by solid, dashed and dotted unit cells. c) Schematic of adatom positions in panel b. d) Atomic model of A[1 1].
9.5.7 \( A[1 \bar{1}] \) and \( A[\bar{1} 1] \)

Figure 9.17a and b show empty state STM images of \( A[1 \bar{1}] \) and \( A[\bar{1} 1] \) respectively. For these boundaries the domains are only shifted parallel to the propagation direction. The domain boundary exhibits two variants indicated with solid and dashed unit cells. Variant 1 (solid) dominates. It has only two adatoms in the AO unit cell which form a \( 1 \times 1 \) arrangement with the top UHUC adatom in the left domain. A large boundary hole forms on either side of the \( 1 \times 1 \) adatoms. The appearance is of a hook. For \( A[1 \bar{1}] \) it points down, and for \( A[\bar{1} 1] \) it points up. In variant 2 (dotted), the adatoms are arranged in the same triangular fashion as a \( 5 \times 5 \) FHUC. This reduces the boundary hole to a small slit. The unit cell drawn with a dashed unit cell matches variant 2 with the top adatom missing.

Structural models for \( A[\bar{1} 1] \) are shown in Fig. 9.17d. For variant 1 (solid), the right adatom is in a conventional \( 5 \times 5 \) configuration bonded to the two adjacent UHUCs through dimers. The left adatom has a \( 1 \times 1 \) arrangement with the right adatom and the top adatom from the left domain. It is bonded to the latter through a dimer. At the bottom of the AO unit cell, two nearest neighbour restatoms saturate the dimer connecting to the lower HUC. One of them also partially satisfies one of the dimer atoms connecting to the left HUC, leaving another with a dangling bond.

Variant 2 is simply a \( 5 \times 5 \) FHUC. The only change is that the dimers connecting to the left domain are staggered: the stacking layer atoms that support the two left adatoms are bonded to different dimers. This leaves one dimer atom and one restlayer atom, situated at opposite ends of the dimer line, unsaturated.

Variant 1 has \( 8 \frac{2}{3} \) dangling bonds per unit cell. Variant 2 has only \( 6 \frac{2}{3} \). On the basis of dangling bond counting variant 2 is expected to be preferred; and yet variant
1 is marginally more frequent. The reason for this contradiction is not clear. Kinetics perhaps plays a role. Variant 2 also contains an unsaturated restlayer atom supporting an adatom, an unusual, and possibly energetically expensive feature.

9.5.8 A[2 2] and A[2 2]

Figures 9.18a and b show empty state STM images of boundaries A[2 2] and A[2 2]. Each image shows two different variants with unit cells demarcated by solid and dashed unit cells. Variant 1 (solid lines) contains three adatoms arranged in the same triangular fashion as a 5×5 HUC. This HUC is in registration with the other unit cells of the right domain, but is misfit from the left domain by the shift vector in a direction parallel to the domain boundary direction. There is only a small boundary hole, which in the images presented here seems to vary in apparent depth. Variant 2 contains only two adatoms. The lower adatom of variant 1 is missing and in its place is a large deep boundary hole. The pattern of adatoms in both variants gives the impression of a graceful S-curve. For variant 1, the curve contains six adatoms, for variant 2, one less.

Structural models for the two variants of A[2 2] are shown in Fig. 9.18d. The unit cell for variant 1 is simply a 5×5 FHUC shifted relative to the left domain. The upper adatom is bonded conventionally across a dimer to the domain on the left. The lower adatom is staggered relative to the opposing dimer and thus leaves a dimer atom and restlayer atom with dangling bonds.

In variant 2 the lower adatom and one of its supporting restlayer atoms are removed. This changes the two remaining restlayer atoms into restatoms and also leaves
dangling bonds on two of the dimer layer atoms. The number of dangling bonds increases by 2 over variant 1. However, this geometry does remove the unsupported restlayer atom present in variant 1.

9.5.9 A[2 1] and A[1 2]

Figure 9.19 shows an empty state image of A[2 1]. This is a rare boundary and this is the only specimen available with good image quality and a reasonably long boundary.
The adatoms in Fig. 9.19a suggest an ideal boundary arrangement. The two domains truncate abruptly at the edge of the unit cell leaving a gap between them. The two domains are, of course, shifted relative to one another, but there is no rearrangement of adatoms on either side of the boundary. The unit cell consists entirely of the narrow, deep trench between the domains.

The atomic model in Fig. 9.19c is consistent with ideally truncated domains. Both domains terminate in a dimer row that, because of the shift, remains unbonded to the other domain. Since each of the four dimers carries two unsaturated bonds, this geometry leaves an extremely high number of dangling bonds within a very small area.


Figure 9.20a and b show empty state images of A[¯¯12] and A[¯¯12]. These boundaries are uncommon, but the few times they have been observed they are always defective and irregular. Panel b alone shows four different unit cells each drawn with a different line type. The adatom arrangement of the short and long dashed unit cells can be derived from that shown with the solid outline. It contains a total of eight adatoms. The left side of the unit cell consists of a triangular 5×5 HUC extended by two adatoms in a 1×1 pattern. On the right side of the cell are another three adatoms arranged in a triangular fashion but shifted vertically from the others. On the left this consists of two 5×5.
Figure 9.20: $A[\bar{2}1]$ and $A[\bar{1}2]$. a and b) Empty state STM images of $A[\bar{1}2]$ and $A[\bar{2}1]$. c) A schematic of adatom arrangements in panel b. c) atomic structure of $A[2\bar{1}]$. 
9.6 B-Type Boundaries

9.6.1 B[\bar{2} 1] and B[\bar{1} 2]

Figures 9.21a and b show empty state images of B[\bar{1} 2] and B[\bar{2} 1]. The two domains both have the same appearance along the boundary: a corner hole ring and two adatoms in a repeating pattern along the boundary. The top domain is shifted in the opposite sense for the two domains, and there are small triangular corner holes lying between the corner holes and the adatom pairs.

An atomic model of B[\bar{2} 1] is shown in Fig. 9.21d. The core unit cell has the shape of an fat “S”, and contains four adatoms arranged in two $3 \times 3$ cells. The selvedge layer of the cell has $180^\circ$ rotational symmetry, broken only by the bulk below. The two central $3 \times 3$ HUCs are completely coordinated to the three adjacent HUCs. The two HUCs on the ends are coordinated completely along only two edges. On the third side the opposing dimer is staggered leaving an exposed dimer atom, and an unsupported stacking layer atom. The tails of the “S”-shaped unit cell contain two opposing and staggered dimers with two dangling bonds each.

9.6.2 B[0 1] and B[\bar{1} 0]

Figures 9.22a and b show empty state images of B[0 1] and B[\bar{1} 0]. These are the only examples of these two boundaries, each about three unit cells long. B[0 1] was observed in the middle of a long boundary of mixed A[0 1] and A[\bar{1} 0]. B[\bar{1} 0] was found between two vertices. The complete corner hole rings on each side of the domain are extended by another three atoms which give a hockey stick appearance. The blades of the opposing hockey sticks straddle a large propeller-shaped boundary hole. The
Figure 9.21: $\text{B}[\overline{2}1]$ and $\text{B}[\overline{1}2]$. a) and b) Empty state STM images of $\text{B}[\overline{1}2]$ and $\text{B}[\overline{2}1]$. c) Schematic of adatom positions in panel b. d) Atomic structure of $\text{B}[\overline{2}1]$
Figure 9.22: **B[01] and B[¯10]**. a and b) Empty state STM images of B[01] and B[¯10]. A tip artifact has caused unusual enhancement of lines running diagonally up and to the right c) Schematic of the adatoms in b. d) Atomic structure of B-10.
hockey stick shaft, and the blades of the propeller point up and to the left for B[01] and up and to the right for B[10]. A second smaller and shallower boundary hole is found between the two corner hole rings.

Figure 9.22 shows a proposed atomic structure for B[10]. The unit cell is a distorted 5×5 cell, with distinct and symmetric faulted and unfaulted halves. The selvedge layer has 180° rotational symmetry which is broken only by the presence of the bulk. Two of the adatoms in each half are bonded to the adjacent HUCs in the conventional manner, competing the corner hole rings at the top and bottom of the boundary. The third adatom, found at either end of the unit cell, bonds to one adjacent HUC, but is displaced from the other. Instead a restatom saturates one of that dimer’s dangling bonds, leaving the other exposed. The restatom, together with the dimer gives the propeller shape to the larger boundary. At the unit cell centre the dimers connecting the faulted and unfaulted HUCs are displaced laterally from one another. This leaves a three-fold coordinated dimer layer atom in each half. This gap, and the restatoms on either side of it, creates the smaller boundary hole between the corner hole rings of the two domains.

9.6.3 B[22]

Figures 9.23a and b show filled and empty state images of a B[22] boundary. This is the single most common type of boundary observed. Such boundaries are long, straight, and free of defects. It will also see that they have important role in patterning adsorbates thanks to their special atomic structure. The unit cell contains 10 adatoms in a local 2×2 arrangement divided into two HUCs. The filled stage images show a contrast difference between the left and right HUCs consistent with faulted and
Figure 9.23: B[22]. a) A possible structure for the B[22] domain boundary.
Figure 9.24: A $7 \times 7$ A$[\bar{2} \bar{2}]$ Domain Boundary. This boundary is found on an island of Ge grown on Si(111)$_{7 \times 7}$. The UC of $5 \times 5$, two HUCs of truncated $7 \times 7$, and the elongated corner hole mirror the motifs found in the $5 \times 5$ boundaries B$[\bar{2} \bar{2}]$ and A$[\bar{2} \bar{2}]$.

unfaulted half asymmetry. Unit cells are separated from one another by a deep, elongated boundary hole.

The structure for B$[\bar{2} \bar{2}]$ is shown in Fig. 9.23e. It essentially comprises of a $7 \times 7$ unit cell with opposite corners truncated. This leaves a boundary hole that is identical in structure to the one in A$[\bar{2} \bar{2}]$. The top and bottom arcs of the boundary hole are each four-adatom fragments of corner hole rings. On each side of the hole there are two dangling bonds from dimer layer atoms supporting the restatom that borders the boundary hole. At the bottom of the hole there are three exposed bulk layer atoms. Aside from the boundary hole details the remainder is identical to the $7 \times 7$ unit cell. In particular each HUC contains three restatoms, in the normal $7 \times 7$ configuration. One of the $7 \times 7$ domain boundaries A$[\bar{2} \bar{2}]$, shown in Fig. 9.24 has similar features.
9.7 Summary

Examples are presented for all of the 14 A-type boundaries, and three of the possible B-type. Eight of the A-type boundaries were observed in both enantiomorphic forms. Some general principles of the atomic structure of the anomalously ordered regions at the boundary core are evident. First, the UHUCs are larger than FHUCs, which consistent with unfaulted stacking having lower energy than the faulted stacking. In almost all cases the boundary has the minimum periodicity allowed by the surrounding domains, $T_A$ in the case of A-type boundaries, and $T_B$ in the case of B-type boundaries. However, $A[22]$ is a noticeable, persistent, and unexplained exception. The most important principle, at least for common boundaries, is that that a boundary’s label does seem to identify a unique atomic structure, although several of the boundaries show variants differing in small ways from one another.
Chapter 10

Vertices

The last chapter examined the detailed atomic structure of 5×5 DAS domain boundaries in the context of the boundary labels introduced in Ch. 8. The focus of this chapter is the meeting of boundaries at vertices. It begins by extending the notation to provide detailed instructions on converting back and forth between standard and shift representations. It then introduces a notation for identifying vertices. With those tools it is possible to simply calculate the relationships between the different boundaries that meet at a vertex. In the next chapter these relationships will be used to explain the distribution of boundaries observed.

10.1 Conversion

Chapter 8 introduced two schemes for identifying a DAS domain boundary. Shift notation indicates the misfit $S_{12}$ between domains 1 and 2, the direction of propagation $T$ in terms of an absolute basis. On the other hand, standard representation identifies a domain boundary according to misfit between the two domains using a basis that
depends on and changes with the orientation of the boundary. Each notation has its advantages: for instance, using shift vectors makes the relationships between boundaries evident (e.g. Eqn. 8.1), but obscures the character of boundary. Fortunately, converting between the two schemes is relatively straightforward.

10.1.1 Converting to Standard Representation

Below is the algorithm to convert a domain boundary with shift vector $S_{12}$ and translation vector $T$ into standard representation.

1. With $T$ arranged so that when viewed from domain 1 it points to the right along the boundary, rotate the coordinate system so that $T' = \pm [1\bar{1}]$ for A-type or $T' = \pm [11]$ for B-type boundaries. The rotation angle $\theta$ will be a multiple of $60^\circ$.

2. If $\theta$ is a multiple of $120^\circ$ then leave the origin where it is. If $\theta$ is $60^\circ$, $180^\circ$, or $300^\circ$ then the new coordinate system no longer has $a_1$ and $a_2$ straddling the UHUC. This can be corrected by rotating the coordinate system $180^\circ$ so that it is aligned correctly, and then moving the origin to domain 2. When combined, these two operations ($180^\circ$ rotation followed by the origin swap) leave $S'$ unchanged.

3. The boundary label in standard representation can be found from the shift vector as $\Lambda = S' = R(\theta)S$

An example of this process is shown in Fig. 10.1. In shift notation with the basis as shown, the boundary has $S_{12} = [\bar{1}2]$ with $T = [10]$. Rotating the basis by $\theta = -60^\circ$ makes $T' = [1\bar{1}]$ and $S' = R(-60^\circ)S = [11]$, but now $a_1$ and $a_2$ straddle the FHUC rather than UHUC. To correct this the origin of the rose is shifted to the
10.1.2 Converting from Standard Representation to Shift Notation

Standard representation sacrifices information in the interest of making the identity of a domain boundary clear from the label. The label indicates whether a boundary is A- or B-type, but it does not specify which of the three possible directions it propagates along. Similarly, the notation does not indicate which domain is the reference domain (i.e. $\Lambda_{12} = \Lambda_{21}$), since that is defined by the right-handed orientation of the truncation vector. Consider a single boundary between two domains 1 and 2 with label $\Lambda$, but with no \textit{a priori} basis. If it is an A-type boundary then the truncation
vector is $\mathbf{T} = \mathbf{T}_A = [1\overline{1}]$, if the boundary is B-type then it is $\mathbf{T} = \mathbf{T}_B = [11]$. This can be used to define the orientation of the new coordinate system. If $\mathbf{T}$, as seen from domain 1, points to the right then $\mathbf{S}_{12} = \Lambda$, otherwise $\mathbf{S}_{12} = -\mathbf{S}_{21} = -\Lambda$. So with an individual boundary the coordinate system is derived from the definition of the propagation direction, and the indices of the shift are taken directly from the label, subject to a possible sign change to account for a switch of origin.

When converting multiple labels the orientation of the coordinate system is defined by the propagation direction of the boundary, but since in shift notation the coordinate system is fixed, the label indices must be rotated to maintain consistency between one another. Essentially the job is to invert the process described in Sec. 10.1.1. In that situation the coordinate system was rotated into a standard alignment, and the reference domain was selected in the only way consistent with that alignment. The choice of reference domain does not have an outward effect on the label since ($\Lambda_{12} = \Lambda_{21}$), but that is not true for shift indices ($\mathbf{S}_{12} = -\mathbf{S}_{21}$). So cases which involve swapping the reference domain invert the indices. Hence the process of converting from standard representation to shift notation involves a combination of rotations by $0^\circ$, $120^\circ$, or $240^\circ$, and inversion.

Figure 10.2 summarizes the operations for converting from standard representation to shift notation in one diagram. The information encapsulated within it will be used repeatedly in this chapter. First, the absolute basis is shown in the upper left. The figure indicates how to convert domain boundary labels into shift notation expressed in that basis. Each of the lines represents a possible domain boundary. Solid lines correspond to A-type boundaries and dashed lines B-type. All possible boundaries are shown. Obviously the boundary type alternates with increasing angle, and each
Figure 10.2: Summary of Standard Representation. The lines on the right indicate the different boundary propagation directions; solid lines indicate A-type boundaries, dashed lines indicate B-type. The schematic unit cell at the upper right shows the basis into which it is desired to convert the boundary labels. The operations written adjacent to each boundary show what to do to make the conversion.

boundary is separated by 30° from the next. The arrows on each boundary show the direction of propagation $\mathbf{T}$ and the ticks mark the reference domain. For each boundary, listed around the perimeter of the figure is the operation required to convert the indices of its label into a shift vector with the reference domain on the clockwise side of the boundary.

The simplest possible example is that of a straight boundary as shown in Fig. 10.3a. This is a single B-type boundary dividing two domains. For the purposes of this example the boundary has been artificially divided into two segments $\Lambda_1$ between domains 1 and 2, and $\Lambda_2$ between domains 3 and 4. If the coordinate system $\mathbf{a}_1$, $\mathbf{a}_2$ is aligned as shown at the bottom of the figure, the shifts for these two domains,
expressed in this basis, are

\[ S_{12} = -R(240^\circ) \Lambda_1, \quad (10.1) \]
\[ S_{34} = R(240^\circ) \Lambda_2. \quad (10.2) \]

But, since \( \Lambda_1 = \Lambda_2 \) then

\[ S_{43} = -S_{34} = -R(240^\circ) \Lambda_1 \quad (10.3) \]

as expected, since domains 1 and 4 and domains 2 and 3 are the same.

A more complicated example, involving three distinct boundaries meeting at a
vertex, is shown in Fig. 10.3b. In standard representation the three boundaries are
B[n m], A[p q], and B[r s]. They converge at an A_{150}B_{120}B_{90}A vertex (this notation will be explained in the next section). In the same basis as the previous example, the three shift vectors are:

\[ S_{12} = -R(0^\circ)A_1 = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} n \\ m \end{bmatrix} = [\bar{n} \bar{m}], \quad (10.4) \]

\[ S_{23} = -R(240^\circ)A_2 = \begin{bmatrix} 0 & 1 \\ -1 & -1 \end{bmatrix} \begin{bmatrix} p \\ q \end{bmatrix} = [q \bar{p} + \bar{q}], \quad (10.5) \]

and

\[ S_{31} = R(0^\circ)A_3 = [r s]. \quad (10.6) \]

Since the sum of the shift vectors around the loop must be zero

\[ S_{12} + S_{23} + S_{31} = 0, \quad (10.7) \]

which means that

\[ 0 = -n + q + r \quad (10.8) \]

and

\[ 0 = -m - p - q + s. \quad (10.9) \]

These expressions place conditions upon the relationships between boundaries that meet at a vertex. This technique, of converting labels to shift vectors and then making use of Eqn. 8.1, will be used extensively in what follows.
Before proceeding further, a notation for identifying vertices is introduced. Consider a boundary divided into two segments JK and KL by a kink at K. Segment JK has character $\Lambda_1 = X[nm]$ and KL has character $\Lambda_2 = Y[pq]$. Angle $\alpha$ is the angle from $\Lambda_1$ to $\Lambda_2$ (i.e. $\angle JKL$) measured counter-clockwise, and $\beta$ is the angle from the angle from $\Lambda_2$ to $\Lambda_1$ ($\angle LKJ$) measured in the same sense. The notation identifies the kink by listing the labels of the segments in a clockwise sequence with the angles interleaved between them. The direction of propagation of each boundary is indicated with a right pointing over-arrow if the boundary runs away from the vertex, and a left pointing one if it runs towards the vertex. Thus Fig. 10.4a shows a $\overrightarrow{X[nm]}_\alpha Y[pq]_\beta \overrightarrow{X[nm]}$ kink. Depending on the context different components can be omitted. Often, the indices and the propagation directions will be left off, leaving only the boundary types; for example $X_\alpha Y_\beta X$ or $A_{300}A_{60}A$.

Vertices, where more than two boundary segments meet, use the same notation.
The three boundary vertex shown in Fig. 10.4b would be called $X_\alpha Y_\beta Z_\gamma X$. Higher order vertices can be constructed by adding further terms. The angles, of course, must sum to $360^\circ$. This notation can be used to describe collections of boundaries even when they do not meet at a common point, or adjacent boundaries lie parallel to one another.

The relationships between A- and B-type boundaries enforce some restrictions between the angles and the boundaries that may appear at kink or vertex. The angle between any two boundaries must be a multiple of $30^\circ$, so $\theta = i \times 30^\circ$ where $i$ is an integer. If both boundaries are the same type then $i$ is even, otherwise $i$ is odd. The definition of standard representation also dictates the allowed directions. If two boundaries $X$ and $Y$ are separated by angle $\alpha$, $X_\alpha Y$, then the type and direction of $Y$ is completely determined by the type and direction of $X$ and the angle $\alpha$, as summarized in the table below, based on Fig. 10.2.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$X$</th>
<th>$\vec{A}$</th>
<th>$\vec{B}$</th>
<th>$\vec{A}$</th>
<th>$\vec{B}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$30^\circ$</td>
<td>$\vec{B}$</td>
<td>$\vec{A}$</td>
<td>$\vec{B}$</td>
<td>$\vec{A}$</td>
<td></td>
</tr>
<tr>
<td>$60^\circ$</td>
<td>$\vec{A}$</td>
<td>$\vec{B}$</td>
<td>$\vec{A}$</td>
<td>$\vec{B}$</td>
<td></td>
</tr>
<tr>
<td>$90^\circ$</td>
<td>$\vec{B}$</td>
<td>$\vec{A}$</td>
<td>$\vec{B}$</td>
<td>$\vec{A}$</td>
<td></td>
</tr>
<tr>
<td>$120^\circ$</td>
<td>$\vec{A}$</td>
<td>$\vec{B}$</td>
<td>$\vec{A}$</td>
<td>$\vec{B}$</td>
<td></td>
</tr>
</tbody>
</table>

Since the surface has $C_3$ rotational symmetry, the sequence repeats after $120^\circ$. So, for instance $\vec{A}_{300} \vec{A}_{60} \vec{A}$ and $\vec{A}_{270} \vec{B}_{90} \vec{A}$ are both valid kinks, but $A_{300}B_{60}A$, $A_{270}A_{90}A$, and $\vec{A}_{300} \vec{A}_{60} \vec{A}$ are not.

The order of the segments is important, but the list is cyclic, so $A_{270}B_{90}A$ is equivalent to $B_{90}A_{270}B$, and $A_{180}A_{90}B_{90}A$ is the same as $A_{90}B_{90}A_{180}A$. In general,
the sequence will be arranged so that the largest angle appears first.

10.2.1 Vertex Classes and the Plane Isometries

All vertices can be segregated into classes whose members have the same angles between boundaries, but different boundary types and orientations. The members are found by permuting the order of the angles and the type of the boundaries, subject to the restrictions imposed by the notation. For kinks (2-vertices) and 3-vertices the complete class can be built from permutations that correspond to plane rotations and reflections. Here, they are presented in the notation introduced in the previous section. They can, however, also be written in a particularly elegant form using complex numbers. This alternate form is shown in Appx. C.

Rotation

The smallest rotation consistent with the boundary propagation directions is by $30^\circ$. Higher angle rotations can be built from successive applications of this smallest rotation. The first important effect of a $30^\circ$ rotation is that it switches the type of all the boundaries in the vertex. So A-type boundaries become B-type, and B-type become A-type. Also, if the boundary is originally A-type then the direction of $T$ is reversed (i.e. $\overrightarrow{A} \xrightarrow{R(30^\circ)} \overrightarrow{B}$, but if it is B-type then the direction remains unchanged (i.e. $\overrightarrow{B} \xrightarrow{R(30^\circ)} \overrightarrow{A}$).

Repeated $30^\circ$ rotations build up the higher angles. Since the surface has $120^\circ$ rotation symmetry the cycle repeats itself after $120^\circ$. These relationships are derived from those that govern the type and direction of different boundaries within a vertex, as summarized in Fig. 10.2.
CHAPTER 10. VERTICES

<table>
<thead>
<tr>
<th>Rotation</th>
<th>( \vec{A} )</th>
<th>( \vec{B} )</th>
<th>( \vec{A} )</th>
<th>( \vec{B} )</th>
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</thead>
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<td>30°</td>
<td>( \vec{B} )</td>
<td>( \vec{A} )</td>
<td>( \vec{B} )</td>
<td>( \vec{A} )</td>
</tr>
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<td>( \vec{B} )</td>
<td>( \vec{A} )</td>
<td>( \vec{B} )</td>
</tr>
<tr>
<td>90°</td>
<td>( \vec{B} )</td>
<td>( \vec{A} )</td>
<td>( \vec{B} )</td>
<td>( \vec{A} )</td>
</tr>
<tr>
<td>120°</td>
<td>( \vec{A} )</td>
<td>( \vec{B} )</td>
<td>( \vec{A} )</td>
<td>( \vec{B} )</td>
</tr>
</tbody>
</table>

So, for example rotating

\( \vec{B}_{150} \vec{A}_{120} \vec{A}_{90} \vec{B} \)

by 90° results in

\( \vec{A}_{150} \vec{B}_{120} \vec{B}_{90} \vec{A} \).

Reflection

Reflections in axes aligned along \( T_A \) or \( T_B \) preserve the boundary type. However, the direction of the propagation direction relative to the vertex centre will change depending on the misalignment between the reflection axis and the boundary. For reflection in an axis misaligned by \( \phi = i \times 30° \) the propagation direction will be reversed if \( i \) is odd, otherwise it remains the same. Since the boundary type alternates with 30° steps, upon reflection in an A-type axis the propagation direction reverses for any B-type boundary, but remains the same for A-type boundaries. The opposite is true for reflections in B-type axes.

<table>
<thead>
<tr>
<th>Axis</th>
<th>( \vec{A} )</th>
<th>( \vec{B} )</th>
<th>( \vec{A} )</th>
<th>( \vec{B} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( \vec{A} )</td>
<td>( \vec{B} )</td>
<td>( \vec{A} )</td>
<td>( \vec{B} )</td>
</tr>
<tr>
<td>B</td>
<td>( \vec{A} )</td>
<td>( \vec{B} )</td>
<td>( \vec{A} )</td>
<td>( \vec{B} )</td>
</tr>
</tbody>
</table>

For a vertex, reflection in any of the boundaries which compose it switches the
Reflect in A

Figure 10.5: Vertex Reflection. Reflecting the vertex $\overrightarrow{B}_{150} \overrightarrow{A}_{120} \overrightarrow{A}_{90} \overrightarrow{B}$ in the first A-type boundary (shown by the broad grey line) results in the vertex shown on the right, $\overrightarrow{A}_{150} \overrightarrow{B}_{90} \overrightarrow{A}_{120} \overrightarrow{A}$.

sequence of the other boundaries and angles about that boundary. So, for instance as shown in Fig. 10.5, reflection in the first A-type boundary of

$\overrightarrow{B}_{150} \overrightarrow{A}_{120} \overrightarrow{A}_{90} \overrightarrow{B}$

yields

$\overrightarrow{A}_{120} \overrightarrow{A}_{150} \overrightarrow{B}_{90} \overrightarrow{A}$,

which when written conventionally, with the largest angle first, is

$\overrightarrow{A}_{150} \overrightarrow{B}_{90} \overrightarrow{A}_{120} \overrightarrow{A}$.

Enumerating Vertices

For kinks the complete class can be constructed by repeatedly rotating by 30° any member of the class. Thus, every class of kinks contains four members. Reflections for kinks do not generate new class members since they can be composed of rotations. This is because a bent line on a plane, the outline of the boundary, is mirror
symmetric. The class for 30° kinks, for example, is

<table>
<thead>
<tr>
<th>30°</th>
<th>[\overrightarrow{A}<em>{210} \overrightarrow{B}</em>{150} \overrightarrow{A}]</th>
</tr>
</thead>
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<tr>
<td></td>
<td>[\overrightarrow{B}<em>{210} \overrightarrow{A}</em>{150} \overrightarrow{B}]</td>
</tr>
<tr>
<td></td>
<td>[\overrightarrow{A}<em>{210} \overrightarrow{B}</em>{150} \overrightarrow{A}]</td>
</tr>
<tr>
<td></td>
<td>[\overrightarrow{B}<em>{210} \overrightarrow{A}</em>{150} \overrightarrow{B}]</td>
</tr>
</tbody>
</table>

For 3-vertices the outline of boundaries with two or more equal angles is also achiral, and such classes have only four members corresponding to rotations. The most symmetric class \((\alpha = \beta = \gamma)\) is

<table>
<thead>
<tr>
<th>X^{120}X^{120}X^{120}X</th>
<th>[\overrightarrow{A}<em>{120} \overrightarrow{B}</em>{120} \overrightarrow{A}_{120} \overrightarrow{B}]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[\overrightarrow{B}<em>{120} \overrightarrow{B}</em>{120} \overrightarrow{B}]</td>
</tr>
<tr>
<td></td>
<td>[\overrightarrow{A}<em>{120} \overrightarrow{A}</em>{120} \overrightarrow{A}]</td>
</tr>
<tr>
<td></td>
<td>[\overrightarrow{B}<em>{120} \overrightarrow{B}</em>{120} \overrightarrow{B}]</td>
</tr>
</tbody>
</table>

Observations illustrating that \[\overrightarrow{B}_{120} \overrightarrow{B}_{120} \overrightarrow{B}\] and \[\overrightarrow{B}_{120} \overrightarrow{B}_{120} \overrightarrow{B}\] are indeed distinct entities are presented in Sec. 10.4.3. is demonstrated by Fig. 10.19.

For 3-vertices whose outlines lack mirror symmetry, reflections do generate new members, and these classes contain 8 members. The class for \(X_{240}X_{90}Y_{30}X\) is
Complete lists of all possible kinks and 3-vertices are presented in Appx. C. There are 20 unique kinks and 72 3-vertices, without consideration of the character of the boundaries which make the vertex. For kinks there are 24 possible choices of character for each vertex, and for 3-vertices there are 552 \((= 24 \times (24 - 1))\). Thus, when boundary indices are included there are 480 possible types of kink, and 39744 possible vertices. The point is that even though the rules for boundaries meeting are simple, there are many different ways that this can happen, and yet later sections will show that, relatively few of the possibilities seem to appear in practice.

In the following sections we will use vertex notation to identify structures, and use the loop sum rule to define the relationships between the characters of the boundaries that define them.

### 10.3 Kinks

Fig. 10.6 illustrates the five classes of domain boundary kinks. We will start by focussing on the \(X_{210}Y_{150}X\) class which have the smallest boundary deflection. For simplicity we will refer to it as a 30° kink, according to its angle of deflection. Higher angle kinks can be built up as successive kinks of this type.

In Fig. 10.7 two domains 1 and 2 are separated by a boundary with three segments
Figure 10.6: The Five Kink Classes. The dashed and solid lines indicate boundaries of different type.

Figure 10.7: A Series of Kinks. The segment $B[nm]$ undergoes a $30^\circ$ kink at $K_1$ into segment $A[pq]$, which subsequently kinks into $B[rs]$. $K_1$ is a $\overline{B_{210}}\overline{A_{150}}\overline{A}$ vertex.
and kinks at K1 and K2. For concreteness we will say that the first segment is \( \overrightarrow{B[nm]} \), but it will soon be clear that the results of the analysis are the same when started with boundaries of any type and orientation. This makes K1 a \( \overrightarrow{B_{210}A_{150}B} \) kink and K2 a \( \overrightarrow{A_{210}B_{150}A} \) kink. Notice that the sense of the A-type boundary is different for the two vertices. At K1 the boundary kinks from \( B[nm] \) into \( \overleftarrow{A[pq]} \). By referring to Fig. 10.2 and following the procedures used in Sec. 10.1.2 both labels can be converted to shift notation:

\[
S_{12} = [nm] \quad (10.10)
\]
and

\[
S'_{21} = -R(120)[pq] = \begin{bmatrix} 1 & 1 \\ -1 & 0 \end{bmatrix} \begin{bmatrix} p \\ q \end{bmatrix} = [p + q - p]. \quad (10.11)
\]

Since \( S_{12} + S'_{21} = 0 \), \( p = m \) and \( q = -n - m \) thus the second segment is \( A[m - n - m] \).

The indices of the third segment can be found in the same way and are \( B[n + m - n] \). Since the change from segment 1 to segment 3 is effectively a \( 60^\circ \) kink this defines the index relationship for a \( \overrightarrow{B_{240}B_{120}B} \) kink. All such relationships are summarized in Fig. 10.8 for kinks up to \( 90^\circ \).

### 10.3.1 Orbits

This procedure can be repeated, kinking \( 30^\circ \) at a time, until the boundary returns to the original \( B[nm] \) segment. The generates a (hypothetical) dodecagonal pocket of domain 2 within domain 1. A numerical example serves to illustrate the point: if the
<table>
<thead>
<tr>
<th></th>
<th>A-type</th>
<th>B-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°</td>
<td>$\overrightarrow{B}[-m,n+m]$</td>
<td>$\overrightarrow{A}[n+m,-n]$</td>
</tr>
<tr>
<td></td>
<td>$\overrightarrow{B}[-n,-m,n]$</td>
<td>$\overrightarrow{A}[m,-n,-m]$</td>
</tr>
<tr>
<td></td>
<td>$\overrightarrow{A}[n,m]$</td>
<td>$\overrightarrow{B}[n,m]$</td>
</tr>
<tr>
<td></td>
<td>$\overrightarrow{B}[n,m]$</td>
<td>$\overrightarrow{A}[n,m,-n]$</td>
</tr>
<tr>
<td>60°</td>
<td>$\overrightarrow{A}[n+m,-n]$</td>
<td>$\overrightarrow{B}[-m,n+m]$</td>
</tr>
<tr>
<td></td>
<td>$\overrightarrow{A}[-m,n+m]$</td>
<td>$\overrightarrow{B}[n+m,-n]$</td>
</tr>
<tr>
<td></td>
<td>$\overrightarrow{A}[n+m,-n]$</td>
<td>$\overrightarrow{B}[n+m,-n]$</td>
</tr>
<tr>
<td>90°</td>
<td>$\overrightarrow{B}[n,m]$</td>
<td>$\overrightarrow{A}[-n,-m]$</td>
</tr>
<tr>
<td></td>
<td>$\overrightarrow{B}[-n,-m]$</td>
<td>$\overrightarrow{A}[n,m]$</td>
</tr>
<tr>
<td></td>
<td>$\overrightarrow{B}[-n,-m]$</td>
<td>$\overrightarrow{A}[-n,-m]$</td>
</tr>
</tbody>
</table>

Figure 10.8: Kink Index Summary. The relationships between different segments that meet at a kink are illustrated for 30°, 60°, and 90° segments. A-type segments are shown as solid lines and B-type as dashed ones. The central segment of each figure can kink into four possibilities. The direction of propagation for each possibility is shown by the arrow. The label indicates the character of the new segment based on the character of the first.
first segment is $B[1 \ 1]$ then the sequence of segments runs

$$B[1 \ 1] \rightarrow A[1 \ 2] \rightarrow B[2 \ \bar{1}] \rightarrow A[\bar{1} \ \bar{1}] \rightarrow B[1 \ 2] \rightarrow A[2 \ 1] \rightarrow$$

$$\rightarrow B[\bar{1} \ \bar{1}] \rightarrow A[\bar{1} \ 2] \rightarrow B[2 \ 1] \rightarrow A[1 \ 1] \rightarrow B[\bar{1} \ 2] \rightarrow A[2 \ \bar{1}] \rightarrow B[1 \ 1].$$

The complete loop is shown in Fig. 10.9c.

This example is a useful reminder of some of the important points about standard representation. Recall that the shift between domains 1 and 2 is the same for every one of these boundaries. However, there are 12 distinct labels that arise through successive kinks. Each one of those will have a different atomic configuration. Thus it illustrates that the details of a domain boundary depend on more than just the shift vector alone.

Also note that the set of labels is closed. Every member of this set is related to every other in that they are a boundary that has the same absolute shift between the two domains. This set is known as the orbit of shifts under the action of rotation group $C_6$. It can be visualized, like in Fig. 10.10, as the points on the shift rose at the corners of a hexagon. We will call this the $[1 \ 1]$ orbit (since both $A[1 \ 1]$ and $B[1 \ 1]$ fall within the same orbit it is not necessary to specify the type). Boundaries can be partitioned into four different orbits: $[1 \ 0], [2 \ 0], [1 \ 1]$, and $[2 \ 1]$. Orbits do not intersect with one another. Since every orbit represents a distinct shift, this means that there are really only four unique ways that one domain can be displaced from a second! Every other differs only in the direction of its propagation. Put another way — any domain boundary could, in principle, assume the character of any of the 11 other boundaries in its orbit simply by kinking. Although in practice this ability is
Figure 10.9: The Four Orbits Shown as a Closed Series of Kinks. Each panel shows a series of equal length boundary segments divided by kinks. The complete boundary closes on itself and separates the enclosed domain (in grey) from the surrounding one. The same absolute shift exists between the two domains exists everywhere, but the label, and hence atomic character, of the boundary changes for each segment. Of course in reality such domain bubbles would not exist — line tension would drive them to shrink and disappear.
Figure 10.10: Shift Rose Showing the Four Orbits. Each shift is linked to another five by 60° rotations, indicated by the inscribed hexagons.

severely restricted it represents an important mechanism in reducing the total energy of domain boundaries.

These 30° kinks are the smallest ones possible and result in the largest possible orbit. Higher angle kinks are simply equivalent to several applications of these minimum kinks. The orbits traveled by the higher angle kinks are subsets of the maximal orbits. For example, for 90° kinks (X_{270}X_{90}X), the [1 1] suborbit is B[1 1]→A[1 1]→B[1 1]→A[1 1]→B[1 1].

10.3.2 Example of Kinks

In practice, the only observed kinks are 30° or 60°. Presumably the higher angle kinks increase the path length too much over a more direct path (see Sec. 11.4.1). Fig. 10.11 shows a sample of 30° kinks. The kinks in Figs. 10.11a&b are a chiral pair. These are common kinks because they are associated with the frequent B[2 2] and A[2 0] boundaries. Less common kinks are shown in c&d.

The atomic structure of the A[0 2]/A[2 0] and B[2 2] boundaries are closely related to one another, differing effectively only in the relative placement of adjoining unit
Figure 10.11: Images of $X_{210}Y_{150}X$ Kinks. a&b) Kinks involving the common $B[22]$ and $A[20]$ boundaries. The two are mirror images of one another. The highlighted unit cells show the kink core. c) two kinks in an $A[11]$ boundary allow it to jog parallel to its direction of propagation: the $A_{210}B_{150}A$ kink cancels the effect of the $A_{210}B_{150}A$ one.
Figure 10.12: Atomic Structure of B[2 2] 30° Kinks. A small section of B[2 2] is shown near the centre. It kinks to the left into A[20], on the right A[02]. The two core UCs are outlined. They share characteristics of both types of boundaries.

Figure 10.13: Schematic of B[2 2] 30° Kinks. The four distinct A_{210}B_{150}A kinks involving B[2 2] and A[20]/A[02]. Shaded and open unit cells represent UHUCs and FHUCs of truncated 7×7. The kink core which links the two boundaries, and is always an UHUC, is shown highlighted. None of the four kinks can be converted into another by rotations and translations.
cells and the details of the boundary hole. Therefore when they meet at a kink the
two boundaries mesh well. The structure of two such kinks is shown in Fig. 10.12.
For both of them a single quasi-7×7 HUC which has the character of the A-type
boundary hole on one side and B-type boundary hole on the other. This kink core
links the two boundaries together. The full array of all four kinks of this class are
shown as schematics in Fig. 10.13, each one of these has a unique, but related, atomic
structure.

Figure 10.14 shows several 60° kinks. There is more variety to this class because
it involves two boundaries of the same type and there is more diversity in A-type
boundaries.

10.4 Vertices

When three domains come together the three corresponding boundaries meet at a ver-
tex. We will deal explicitly with only three-boundary vertices, but the same principles
can be applied to vertices involving more boundaries.

10.4.1 Static Stability

Since boundaries exert line tension, and a vertex will move under the influence of
that tension, only vertices for which that tension in 2D is balanced will be statically
stable. For a vertex $X_\alpha Y_\beta Z_\gamma X$ the condition for static stability requires that

$$\alpha \leq 180^\circ$$

$$\beta \leq 180^\circ$$

(10.12)  
(10.13)
Figure 10.14: Images of $A_{240}A_{120}A$ Kinks.
Figure 10.15: Stable 3-Member Vertex Classes. The top three vertex classes are mirror-symmetric, the bottom three are not. The solid and dashed lines indicate boundaries of opposite type.

and

$$\alpha + \beta \geq 180^\circ$$

(10.14)

The six classes of vertices which pass this test are shown in Fig. 10.15. This restriction is very loose; for instance it includes vertices like $X_{180}X_{90}Y_{90}X$ for which the tension in the Y-type boundary must be infinitesimal. However, it does effectively discount sharp, heavily unbalanced vertices like $X_{300}X_{30}Y_{30}X$, which are never observed.

The examples in Fig. 10.15 have been arranged into two groups, with symmetric ones at the top and asymmetric ones on the bottom. Only two of the vertices ($X_{120}X_{120}X_{120}X$ and $X_{180}X_{120}X_{60}X$) permit all three boundaries to be of the same type.
10.4.2 General Properties

In general, member of a vertex class will have different relationships between the labels of their boundaries. The exception is for vertices that are related by 180° (or equivalently 60°) rotation, for example $\vec{A}_{150} \vec{B}_{150} \vec{A}_{60} \vec{A}$ and $\vec{A}_{150} \vec{B}_{150} \vec{A}_{60} \vec{A}$. Since such a rotation changes the direction, and hence sign of all the boundaries involved the index relationship will be the same for both entities, even though they are different structures. A complete list of all classes and their index relationships, including those which are statically unstable, can be found in Appx. C.

10.4.3 $X_{120}X_{120}X_{120}$ Vertices

The class of equiangular 120° vertices includes four members, corresponding to all A-type or all B-type, with propagation directions either all outwards or all inwards.
Say the three boundaries in Fig. 10.16a are A-type and have labels $A_{12} = \overrightarrow{A}[nm]$, $A_{23} = \overrightarrow{A}[pq]$, and $A_{12} = \overrightarrow{A}[rs]$. These can be converted to shift notation in the manner shown in Sec. 10.1.2 to give:

$$S_{12} = [nm],$$

$$S_{23} = R(120^\circ)[pq] = [-p - q p]$$

and

$$S_{31} = R(-120^\circ)[rs] = [s - r - s].$$

Since the sum of the shifts around the loop must equal zero

$$0 = S_{12} + S_{23} + S_{31} = [nm] + [-p - q p] + [s - r - s]$$

so

$$0 = n - q - p + s$$

and

$$0 = m - r - s + p.$$ 

These describe the restrictions on $A_{23}$ and $A_{31}$. Since the type is the same for all three boundaries, and the boundary outline possesses reflection symmetry, all four members of the class have the same index relationships.

If $p = s$ and $q = r$ then $n = q$ and $m = r = q$. If this happens for A-type boundaries then two of the boundaries, $A[pq]$ and $A[qp]$, are enantiomorphs the third, $A[qq]$ is achiral.

Fig. 10.17 shows a collection of STM images of these sorts of boundaries.
Figure 10.17: Mixed A-Type Equiangular Vertices.
Equiangular and Equi-indicial

As a special case, consider $\Lambda_{23} = \Lambda_{12}$, i.e. both are the same kind of boundary. If this is true then

$$r = n \quad \text{and} \quad s = m.$$  \hspace{1cm} (10.21)

If any two boundaries in a $120^\circ$ vertex are the same then the remaining boundary must also be the same. So such vertices are not only equiangular, but equi-indicial as well. Again, this holds true for both A- and B-type boundaries. Figure 10.18 shows filled and empty state images of a vertex of three $A[20]$ boundaries. The vertex core consists of a single UHUC of $7 \times 7$. The common $B[22]$ boundary also forms equiangular, equi-indicial vertices. Figure 10.19 shows filled and empty state images of a $B_{120}B_{120}B_{120}$ core. Again, the vertex core is a HUC of $7 \times 7$, in this case of faulted stacking. Figure 10.20 shows two such vertices, one centripetal like the last example, and one centrifugal $B_{120}B_{120}B_{120}$ with the boundaries directed inwards. One can be created by rotating the other by $60^\circ$ (or $180^\circ$). For both, the vertex core is a HUC.
Figure 10.19: Filled and Empty State Images of a $B[\bar{2}2]$ $\bar{B}_{120} \bar{B}_{120} \bar{B}_{120} \bar{B}$. The three $B[\bar{2}2]$ boundaries meet at a single FHUC of $7 \times 7$. The faint outline highlights HUCs in both images.

Figure 10.20: Centripetal vs. Centrifugal B-Type Equiangular Vertices. The two vertices differ in their orientation by $60^\circ$, and thus the faulting of their $7 \times 7$ HUC core.
Figure 10.21: A $B[\bar{2}2]$ network. On the left is an STM image showing six long $B[\bar{2}2]$ boundaries converging at four vertices. In the schematic on the right UHUCs are shown dark and FHUCs light. Two of the vertex cores (dark outlines) are FHUCs and two are UHUCs.

of $7\times7$. However, for the centripetal vertex the core is a FHUC, for the centrifugal one it is an UHUC. Thus, even though the vertices are composed of boundaries of the same character, arranged at the same angles, their cores are distinctly different and dependent on the direction of the boundaries.

Because the $B[\bar{2}2]$ boundary is very common it is not unusual to encounter dense tangles of boundaries knit together with vertices of this type. Figure 10.21 shows an example. Here six long $B[\bar{2}2]$ boundaries meet at four vertices, two with FHUC cores and two with UHUC. The cores themselves are closely aligned, separated by only a single unit of boundary. This motif is taken to the extreme in Fig. 10.22 which shows a fanciful kagome-like network of $7\times7$ HUCs. The nearest neighbour spacing between $7\times7$ HUCs of the same faulting would be $\sim8.5$ nm, $4\frac{2}{5}$ the $5\times5$ spacing.
Figure 10.22: A Hypothetical Kagome Lattice of $B[\bar{2}2]$ Boundaries. The bold triangles are complete HUCs of $7\times7$. The truncated triangles which connect them are the incomplete HUCs of $B[\bar{2}2]$. The empty hexagons are contiguous domains of $5\times5$.

Figure 10.23: $X_{150} Y_{150} X_{60} X$ Vertices.
**Figure 10.24: X_{180}X_{90}Y_{90}X Vertex.** The leading boundary of the vertex label (in this case $\vec{B}$) is indicated by the dot.

### 10.4.4 $X_{150}Y_{150}X_{60}X$

Vertices of this class are shaped like a Y, with the boundary that makes the stem of the Y of one type, and the two arms of the opposite type. This class has four members whose index relationships are illustrated in Fig. 10.23. In practice this vertex is very rare — Fig. 10.24 is one of the few examples. However, it will be discussed more in Sec. 11.6.1 in the context of topological transformations.

### 10.4.5 $X_{180}X_{90}Y_{90}X$

These vertices are shaped like a T, with the two colinear boundaries that make the top of the T of one type and the stem of the T the opposite. This vertex class also has four members. The index relationships are shown in Fig. 10.27. The $A_{180}A_{90}B_{90}A$ vertices are more common because of the infrequency of B-type boundaries. Several
examples of such vertices are shown in Fig. 10.26. The first example is an interesting one. In that case $n = p$ and $m = q$, so the two collinear A-type boundaries that make the top of the “T” are enantiomorphs. When that is true $r = -s = n - m$, so the B-type boundary that makes the stem of the “T” is achiral. Here is shown the chiral pair $A[02]$ and $A[20]$ with achiral $B[22]$. When we begin discussing line tension it will be clear that the component of tension exerted at the vertex and directed along the A-type boundaries is zero. Thus the vertex is balanced in that direction.

10.4.6 $X_{180}X_{150}Y_{30}X$

This is the first of the asymmetric vertex classes. Again, the two collinear boundaries are of the same type and the intersecting boundary is of the opposite type. It has eight members whose index relationships are shown in Fig. 10.27. This is an uncommon vertex, two examples are shown in Fig. 10.28. In both cases the two collinear boundaries are A-type, and the single B-type boundary is $B[22]$. 

Figure 10.25: $X_{180}X_{90}Y_{90}X$ Index Relationships.
Figure 10.26: $X_{180}X_{90}Y_{90}X$ Examples. The top left example has interesting nume-rological properties: the two A-type boundaries are chiral enantiomorphs, and the B-type boundary is achiral.
Figure 10.27: $X_{180}X_{150}Y_{30}X$ Index Relationships.
10.4.7 \( X_{180}X_{120}X_{60} \)

There are eight members to this vertex class, but because all three boundaries are the same type there are only two index relationships, as shown in Fig. 10.29. Examples of these vertices are shown in Fig. 10.30.

10.4.8 \( X_{150}Y_{120}Y_{90}X \)

These vertices consist of two boundaries of one type, and one of the opposite. There are eight members of the class. Their index relationships are shown in Fig. 10.31. This is the most common type of vertex, examples of the form \( X_{150}Y_{120}Y_{90}X \) are shown in Fig. 10.32, the mirror form \( X_{150}Y_{90}Y_{120}X \) is shown in Fig. 10.33.

10.5 Vertex Cores

In the previous chapter we proposed that the conditions that defined a domain boundary, encapsulated in its label, were sufficient to identify the atomic configuration of the boundary itself. We found that, generally speaking, this was a reasonable assertion,
Figure 10.29: $X_{180}X_{120}X_{60}X$ Index Relationships.
Figure 10.30: $X_{180}X_{120}X_{60}X$ Examples.
Figure 10.31: $X_{150}Y_{120}Y_{90}X$ Index Relationships.
Figure 10.32: $X_{150} Y_{120} Y_{90} X$ Examples.
Figure 10.33: $X_{150}Y_{90}Y_{120}X$ Examples.
and that a boundary’s label did indeed specify its character. In principle this should be true of vertices too. In this case the “boundary conditions” which determine the solution within the core are the atomic configurations of the boundaries which comprise the vertex. Since they in turn depend on their labels, specifying the labels and arrangement of the converging boundaries ought to define the atomic configuration of the core itself.

It is difficult to judge how well this holds based on the data in hand. Principally, this is a problem of statistics stemming from the dimensional difference between boundaries and vertices. Boundaries are 1D objects, where each unit cell of the boundary represents another sample, whereas vertices are 0D for which another sample requires finding another vertex of the same sort. Thus, surface with large domains generate lots of information on the configuration of boundaries, but orders of magnitude less about the vertices where they meet. This is compounded by the vast number of unique vertices; since most of them have only been observed once, with no opportunity for comparison. However, the principle does seem to hold true for those vertices which involve well-ordered boundaries that appear commonly. The best examples are B[2 2]_{210}A[2 0]_{150}B[2 2] kinks (Fig. 10.11), and the A[2 0] and B[2 2] equiangular vertices.

10.6 Summary

Algorithms for converting between shift and label notation allow the identity of a boundary to be expressed in two different ways. A notation was introduced to identify different vertices and, making use of the loop sum rule, relationships were constructed between the label indices of boundaries that meet at vertices. The following chapter
will make use of these results and use them in an attempt to identify the origin of
the unusual distribution of boundary characters for 5×5.
Chapter 11

The DAS DB Network

Chapter 9 examined individual domain boundaries, and Ch. 10 investigated the relationships between boundaries when they meet. In this chapter, the evolution of domain boundaries will be considered collectively, as a network. The chapter starts by showing that the distribution of domain boundary characters is not uniform but is strongly peaked towards particular species. The remaining sections will attempt to explain, through model cases, the processes that might lead to this asymmetric distribution. It concludes with a brief look at the kinetic restrictions to domain boundary movement.

11.1 Boundary Character Distribution

To better understand the relative energies of the different characters of domain boundaries, a statistical analysis was undertaken. Domain boundaries were examined in STM images and the length of each segment was binned according to its character.
### Table 11.1: Domain Boundary Frequency Data.

Observed frequency values for the possible domain boundaries with A-type on the left and B-type on the right. The values given are the total number of unit cells of each character observed. For A-type boundaries a unit cell is $5a_o$ long, for B-type boundaries it is $\sqrt{3}5a_o$.

<table>
<thead>
<tr>
<th></th>
<th>A-type</th>
<th></th>
<th>B-type</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A[22]$</td>
<td>41</td>
<td>$B[22]$</td>
<td>4</td>
</tr>
</tbody>
</table>

Total=1509 uc (2900 nm)  
Total=969 uc (3222 nm)
Figure 11.1: Boundary Distribution. The distribution of domain boundaries for A-type (left) and B-type (right) boundaries. The bins are arranged by index according to the shift rose (Fig. 8.2). Recall that for A boundaries the [1 1] line is a mirror axis, so A[0 2] and A[2 0], for instance, are enantiomorphs. The intensity scale is logarithmic with black indicating the highest count, and white the lowest. Different scales are used for the two histograms: the B[2 2] boundary is approximately 7 times more common than A[0 2].

Depending on the quality of the images, the character of the boundary segments was assessed by explicitly measuring shift, identifying the appearance of the atomic structure, or deducing the character from adjacent boundaries. The samples selected for this analysis were very close to the 1BL Ge target coverage. Therefore, the terraces in the samples examined were wide (>100 nm), and voids were few. No one boundary traversed an entire terrace, or connected two voids. However, boundaries were included even when they adjoined step edges or defects. In all, some 6350 nm of boundaries are included, taken from images collected on three different samples prepared identically, in the manner described in Sec. 5.6.

Tables 11.1 show the frequency of each of the types of domain boundaries. The same data shown graphically, as an intensity histogram, can be seen in Fig. 11.1.
Figure 11.2: Bar Histogram of A-type Boundaries. The top four bars show the frequency of achiral A boundaries. The remaining bars show, back-to-back, the prevalence of pairs of chiral enantiomorphs.
Some idea of the uncertainties for these values can be had by considering Fig. 11.2 which compares the frequency of A-type chiral pairs. In theory, since there is no energetic difference between such pairs, and if there are no kinetic restrictions to their formation, then each enantiomorph should appear as often as its pair, subject only to statistical uncertainty. In practice, the agreement between enantiomorphs is good, although there is a notable, and unexplained discrepancy between the number of A[1 1] and A[1 1] boundaries. For the three most common pairs, A[0 2], A[0 2], and A[2 2] the average discrepancy is 10%. This is comparable to the uncertainty expected from Poisson statistics, and represents an upper bound to the quantitative accuracy of this analysis.

In total, A-type boundaries make up 46% of all boundaries by length, and B-type 51%. For the remaining 4% of boundaries it was not possible to assess a direction or index. Remarkably, almost all of the B-type boundaries are of the same kind, B[2 2]. In fact, boundaries of that character alone make up 47% of all observations! The dominant A boundaries are A[1 1], A[0 2]/A[2 0], A[0 2]/A[2 0], and A[2 2]/A[2 2]. Together, these seven make up 30% of all boundaries by length.

The results can be divided into the four orbits. Recall that members of an orbit are related to one another through kinks. The table below shows the breakdown by length.

<table>
<thead>
<tr>
<th>Orbit</th>
<th>[1 0]</th>
<th>[1 1]</th>
<th>[2 0]</th>
<th>[2 1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (nm)</td>
<td>514</td>
<td>624</td>
<td>4631</td>
<td>594</td>
</tr>
<tr>
<td>Percent (%)</td>
<td>8</td>
<td>10</td>
<td>73</td>
<td>9</td>
</tr>
</tbody>
</table>

This is reproduced as the pie chart at the centre of Fig. 11.3. The orbits [1 0], [1 1], and [2 1] each contain 8-10% of the total boundary length. By far the dominant
orbit is [20], which includes the remaining 72%. All of the A-type boundaries in the orbit are abundant, and of the top eight most frequent boundaries only A[11] is not in this orbit. The A-type boundaries in this orbit alone (even without B[22]) make up 25% of the total observed length. The effect of kinking at least partially explains the frequency of A[20] and A[02] which the dominant B[22] boundary can become through 30° kinks. Images of such kinks were presented in Fig. 10.11. However, the important point is that kinking alone cannot explain the distribution of orbits, because kinking cannot move counts from one orbit to another.

These histograms indicate several important things. First and most strikingly, the distribution of boundaries is non-uniform. The initial distribution, before annealing, of boundaries is expected to be uniform since domain nucleation happens independently. That the distribution after annealing has become so peaked we take to indicate that the preferred boundaries are energetically favoured over those that are not. The reasons for that energetic preference have been postulated in Ch. 9, but a more precise understanding must await, so far unfeasible, \textit{ab initio} model calculations.

Having postulated that the preference reflects energetic differences among the boundaries, the remainder of this chapter identifies processes by which the network of boundaries might evolve from an initially uniform distribution to the one we observe in Fig. 11.1. So this will be a discussion not so much of why, but how. Even within that limited mandate the results are only speculative sketches.
The pie chart in the centre shows the frequency of each orbit. Clearly, the [2 0] orbit dominates. Each of the panels show the frequency of different boundary characters divided by orbit. Adjacent boundaries are related to one another by 30° kinks. So, for instance, a B[2 2] boundary can kink into either A[2 0] or A[0 2]. Again, the intensity scale is logarithmic, and the intensity for B-22 is clipped to better accentuate the other boundaries.
11.2 Line Tension and Network Energy

Domain boundaries are only kinetically stable. The minimum energy reconstructed surface is the one with no domain boundaries. For $5 \times 5$ this is demonstrated by the fact that long high temperature annealing removes, rather than introduces, boundaries. The free energy of a domain boundary is

$$E = \gamma s$$

(11.1)

where $\gamma$ is the boundary’s line energy and $s$ is its length. Since boundaries are kinetic features the line energy is always positive. The important distinction of domain boundaries is that, like step edges, or crystal faces, their energy is a function of the boundary’s character. So for a boundary made of several segments of different character with lengths $s_i$ and corresponding line energies $\lambda_i$ the total energy is

$$E = \sum_i \gamma_i s_i.$$  

(11.2)

The basic principle under which we will operate is that the network of boundaries evolves to minimize $E$, and that to do so it may evolve in a way that does not necessarily minimize $s$.

Equation 11.2 is an approximation. First, it assumes that the line energy is well defined, while in practice it must vary with the detailed atomic configuration, which as seen in Ch. 9, can vary considerably for some boundaries. However, for long boundaries this can be expected to average out. The expression also neglects the energy of 0D features like boundary kinks and vertices. To account for these, additional terms must be added for each of the vertex types and their frequency.
These corrections will be discussed later in the chapter, but for the moment we will focus only on the line tension.

11.3 Domain Boundaries and Foams

Domain boundaries and soap bubble foams bear strong resemblances to one another. In a dry 2D foam, cells are separated from one another by thin soap films called edges which meet at vertices. On a surface the domains resemble cells, and the boundaries edges. Both foams and domain boundaries are kinetically stable structures that evolve to minimize the total energy of the structure as a whole.

Because there is a substantial literature on the physics of foams it is natural to draw some comparisons with domain boundaries. However, in several important ways foams and domain boundaries differ substantially from one another. These include: the presence of pressure, the uniformity of the surface tension, isotropy of edge directions, and the result of face coalescence. This section will contrast the differences between the well known discipline of foam physics and the relatively unexplored field of domain boundaries. In doing so it will serve as an introduction to the larger chapter which will focus on the processes which drive the evolution of the domain boundary network, and where the practice of contrasting the behaviour of foams to domain boundaries will continue.

A foam can support itself by the pressure of the gas it contains, whereas domain boundaries require an external structure to prevent their collapse. In the simplest case, for a single 2D soap bubble trapped between two plates, the differential free energy is

\[ dE = -PdA + \gamma dl, \]  

(11.3)
where $P$ is the internal 2D-resolved pressure, and $A$ the enclosed area. In equilibrium, the first term balances the second and the bubble is stable with the internal pressure of the trapped air balanced by the surface tension of the bubble envelope. On the other hand the free energy in the case of a boundary “bubble” is always positive. Thus, the equilibrium solution is the one with no surface area at all ($l = 0$).

In a similar way, foams, which are clusters of bubbles, can be self-supporting. For example a froth floating on the surface of a liquid or in air. Domain boundaries networks, however, always require external support at their perimeter from steps, islands, voids, or other defects. In this respect they more closely resemble a spider’s web — without anchor sites the elasticity of the silk causes the web to collapse inwards on itself. In Sec. 7.5 we discussed the effect that the tension exerted by domain boundaries has on the morphology of the steps to which they anchor.

The presence of pressure also has an important effect on the how edge movement propagates. In a foam, changes in a one edge will affect the cell pressure and hence directly affect the other edges of that cell. For domain boundaries, because there is no pressure, the effect of changes to one boundary are mediated through the boundaries that connect to it.

The second important difference between foams and domain boundaries is that in the former the surface tension is fixed, while in the latter it depends on the character of the boundary. In foams this means that edges (and therefore cells) only ever meet three at a time, and since they all exert the same surface tension they make an angle of 120° with one another. This last point is known as Plateau’s law. In the case of a domain boundary however, boundaries of different character, having different line tensions can meet angles very different than 120°.
An edge in a foam is free to assume whatever orientation and path spans the space between its two endpoints with the lowest energy. The most efficient route in this case is a straight line (there is some curvature to cell walls to accommodate the pressure difference between the cells, but for dry foams this is often small). Domain boundaries however are constrained to lie along one of the high symmetry directions. So the most efficient route will not be straight. In fact, since the character dictates the energy, the most efficient route might not even be the shortest path along the symmetry directions.

Finally, the last major difference is the means by which edges and boundaries can appear or disappear. In a foam the meeting of two parallel edges results in their coalescence — what was three cells becomes two. One mode for an edge to disappear is through popping. Neither of these processes is common, but they are possible. For domain boundaries, parallel meeting does generally result in coalescence. But in rare cases, when their character is right, the boundaries can mutually annihilate leaving no boundary at all. Thus, three domains become one. Conversely a domain boundary cannot be "popped"; there is no way to abruptly remove a domain boundary since that would require the kinetically forbidden process of shifting one domain to match the other.

11.4 Direct and Indirect Paths

We begin our discussion on the evolution of the domain boundary network by considering the action of kinking under line tension. In Fig. 11.4 a domain boundary is shown pinned at either end by vertices at points P and Q. If PQ is directed along one of the high symmetry directions the shortest possible segment between PQ will be a
Figure 11.4: Indirect Paths. The shortest boundary between the two points P and Q lying along a high symmetry direction is a straight line. The two indirect paths PR₁Q and PR₂Q follow longer routes involving a kink.

Figure 11.5: Indices of Indirect Paths. The indices of indirect paths for A (left) and B-type (right) direct paths.

pure A or B-type boundary. This is the direct path. However, there are alternate routes to get from P to Q. A multitude of variations are possible, but we will examine only the two shortest such routes, which we will call the upper and lower indirect paths. These are shown as dotted lines in Fig. 11.4; they run along PR₁Q and PR₂Q respectively. In each path the two legs are of equal lengths and are at an angle of 30° from the PQ direction. Both legs have opposite type to the direct path, and undergo a 60° kink at R. The indices of the indirect paths can be found using the procedures established in the last chapter, and are found in Fig. 11.5.

All of the indirect routes involve the boundary travelling a distance $2/\sqrt{3} \times$ longer
Figure 11.6: A Skewed Indirect Path. If the line PQ' is misaligned from a high symmetry line PQ by perpendicular displacement $y$ then the direct path follows PVQ' and the indirect path PRQ'. Which of these paths the boundary adopts depends on the relative line energies of the three different boundaries.

than the direct route. This would only happen if the energy of the longer indirect route was smaller than that of the direct one. If $\lambda_o$ is the line energy of the direct path, and $\lambda_1$ and $\lambda_2$ the energies of PR$_1$ and R$_1$Q then the energy difference, per unit length of PQ, between the direct and indirect and routes is

$$\Delta E = E_o - E_1 = \lambda_o - \frac{1}{\sqrt{3}}(\lambda_1 + \lambda_2).$$

(11.4)

If this is positive the indirect route has a lower energy and will be favoured, if it is negative the direct path is the low energy route. This neglects the expense of the kink itself. The lower indirect route has the same segments just traveled in the opposite order, so its energy is the same. Thus, either of the two indirect routes are equivalent alternatives to the direct route. If it is preferred, the transition from the direct to the indirect path can be accomplished continuously, reversibly, and monotonically through small distortions. Thus, the kinetic barrier is small.
11.4.1 Skewed Indirect Paths and Boundary Rotation

Figure 11.6 illustrates what happens if the endpoints of the direct path do not happen to lie perfectly aligned with a high symmetry direction. If \( PQ' \) is misaligned by the perpendicular offset \( y \) then the direct path itself must kink to meet \( Q' \) and divides into two segments \( PV \), a shorter version of the original direct path, and \( VQ \) which has the same character as the segment \( PR \) of the indirect path. The second important effect is that the two segments of the indirect path no longer have equal length. The lengths of the direct path segments \( PV \) and \( VQ \) are \( t_o \) and \( t_1 \), and the lengths of \( PR \) and \( RQ \) along the indirect path are \( s_1 \) and \( s_2 \). The energies of the two routes are

\[
E_o = \lambda_o t_o + \lambda_n(y)t_1 \quad (11.5)
\]

\[
E_1 = \lambda_1 s_1 + \lambda_2 s_2. \quad (11.6)
\]

The choice of \( \lambda_n \) is determined by the sign of \( y \)

\[
\lambda_n(y) = \begin{cases} 
\lambda_1 & \text{if } y \geq 0 \\
\lambda_2 & \text{if } y \leq 0 
\end{cases} \quad (11.7)
\]

The geometry of the situation reveals that lengths are

\[
t_o = x - \sqrt{3}|y|s_1 = \frac{1}{3}x + y \quad (11.8)
\]

\[
t_1 = 2|y|s_2 = \frac{1}{3}x - y \quad (11.9)
\]
For a distance PQ of \( x = 1 \), the energy difference between the two paths is

\[
\Delta E = E_o - E_1 = \beta - \sqrt{3}\beta y. \tag{11.10}
\]

where \( \beta = \lambda_o - \frac{1}{\sqrt{3}}(\lambda_1 + \lambda_2) \). The sign of the energy difference is determined by \( \beta \), so it determines the relative energy preference for the two routes. The condition then is precisely the same as for the aligned case \( (y = 0) \) examined above.

Figure 11.7 illustrates the path energies as a function of offset for different boundary energies \( \lambda \). The four extreme paths are illustrated in Fig. 11.7a and correspond to I) pure direct path, II) indirect path with equal lengths \( s_1 \) and \( s_2 \), III) indirect path with all \( s_1 \) \( (y = +\frac{1}{\sqrt{3}}) \), and IV) indirect path with all \( s_2 \) \( (y = +\frac{1}{\sqrt{3}}) \). Each of the plots corresponds to a different combination of relative boundary energies. For \( \lambda_o = \lambda_1 = \lambda_2 \) in this case, since the boundaries are all the same the minimum path energy corresponds to the shortest distance between P and Q: path I. If \( \lambda_o = 0 \) and the others remain the same, as shown in c, this is amplified and path I is strongly preferred. If \( \lambda_o \) is instead raised above the critical value of \( 2/\sqrt{3} \) then the indirect route is preferred, but all endpoint offsets give the same energy, as is shown in d. We will return to this degeneracy later. Figures 11.7e shows the case for \( \lambda_1 = 0 \). The lowest energy solution is a pure \( s_1 \) boundary. In f the opposite case is shown. There is no scenario for which path II is the global minimum route.

In cases b, c, e & f there is a distinct geometry with the lowest energy. If the endpoint \( Q' \) is free to move in \( y \), this is the configuration that the boundary will adopt. Thus the boundary will try to straighten and rotate. In practice, any vertex will be restricted by the other two (or more) boundaries attached to it. This vertex drag restricts how effectively the boundary can rotate to adopt the low energy path. So, a
Figure 11.7: The Potential of Indirect Paths. a) The four possible path extremes. b-f) Potentials for direct (black) and indirect (grey) paths, corresponding to different segment line energies. The four extrema indicated correspond to the trajectories shown in a.
boundary will exert a torque on the vertex to which it attaches that, in equilibrium, will be balanced by the torques exerted by the other two boundaries.

The case $d$ represents an interesting situation. Since $\lambda_o > \frac{1}{\sqrt{3}}(\lambda_1 + \lambda_2)$ the indirect path is preferred, but because $\lambda_1 = \lambda_2$ there is no one path that is a global minimum. Thus, any route involving $s_1$ and $s_2$ segments is equally costly. If kink energy is negligible then the path can even include many small segments and the boundary will meander. The character of $s_1$ cannot be the same as that for $s_2$, since they are aligned $60^\circ$ from one another. So, in general the energy of the two segments will not be the same. However, there is a special class of boundaries for which the boundary energy will in fact be identical: enantiomorphs. There are six pairs of boundaries for which a $60^\circ$ kink will transform one enantiomorph into its chiral partner. These, along with the corresponding direct boundary, are shown in Table 11.2.

In practice, examples of meandering are hard to come by. First, the two cases with B-type indirect paths are never observed. For the $A[20]/A[02]$ case the direct path, $B[22]$, is preferred. The $A[\bar{1}0]/A[0\bar{1}]$ boundary is a very rare one, which leaves only $A[10]/A[01]$ and $A[\bar{2}0]/A[02]$. The former is relatively uncommon, and in the specimens observed, is never seen to meander. In this case, perhaps, the kink energy

---

**Table 11.2: Meandering Boundaries.** The direct boundary on the left can be broken into segments of the two characters on the right. Since the pair are enantiomorphs they do not exert a torque.

<table>
<thead>
<tr>
<th>Direct</th>
<th>Indirect</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A[1\bar{1}]$</td>
<td>$B[21]$</td>
</tr>
<tr>
<td>$B[\bar{2}2]$</td>
<td>$A[2\bar{0}]$</td>
</tr>
<tr>
<td>$B[\bar{1}1]$</td>
<td>$A[1\bar{0}]$</td>
</tr>
<tr>
<td>$B[1\bar{1}]$</td>
<td>$A[1\bar{0}]$</td>
</tr>
<tr>
<td>$B[\bar{2}1]$</td>
<td>$A[2\bar{0}]$</td>
</tr>
</tbody>
</table>

---

*CHAPTER 11. THE DAS DB NETWORK*
Figure 11.8: Meandering \( A[2\overline{0}] / A[0\overline{2}] \) Boundaries. The character of each unit cell can be discerned from the pattern made by the adatoms. The shape of \( A[2\overline{0}] \) is a hexagonal corner hole ring with a “step” that hooks to the right. For \( A[0\overline{2}] \) the “stem” hooks to the left.

is significant and drives the boundary to straighten. The final case \( A[2\overline{0}] / A[0\overline{2}] \) is common, and does meander. Some examples are shown in Fig. 11.8.

### 11.5 Topology

The number of cells \( B \), edges \( D \), and vertices \( V \) of a foam are related by the Euler characteristic. For a network of domain boundaries in 2D this means that

\[
D - B + V = 1. \tag{11.11}
\]

Practically speaking the Euler characteristic can be calculated by counting all of the cells, edges, and vertices that are completely contained within a finite loop, rather than the infinite plane.
Figure 11.9: The T1 Process. Moving from left to right the domains 1 and 3 both gain a boundary, and the domains 2 and 4 lose one. The process can also move in the opposite direction.

11.6 Topological Changes

In foam physics there are two possible topological changes that can take place leading to a change in the number of edges to a cell. These are called T1 and T2 [201]. For domain boundary networks topological changes affect boundary character by aggregation or division of vertices. Only these changes can shift the boundary distribution between orbits.

11.6.1 T1

The T1 process is illustrated in Fig. 11.9. Four domains are shown, separated by five boundaries that meet at two vertices. In the process moving from left to right the domains 1 and 3 both gain a boundary, and domains 2 and 4 lose one. When moving in the opposite sense the reverse is true. Importantly, the two vertices change during the transition, and the boundary that lies between them changes as well. The following example illustrates the process.

Figure 11.10a shows an image of what is likely a T1 process frozen in place. In this case two B_{150}A_{150}B_{60}B vertices are separated by a short segment of A[22]. If they
Figure 11.10: a) STM image of two pairs of B[22] boundaries meeting at vertices separated by a short segment of A[22]. b) A schematic of a, which when it undergoes a topological change leads to network seen in c composed entirely of B[22].
were to further approach one another the process shown in Fig. 11.10b&c would take place: the two vertices would become \( B_{120}B_{120}B_{120}B \), and the segment between them would become another \( B[\bar{2}2] \). The \( A[22] \) boundary is rare, so this process succeeds in eliminating an unfavourable boundary and replacing it with a favourable one.

### 11.6.2 T2

Figure 11.11b shows a complex, but symmetric, arrangement of domain boundaries. Three A-type boundaries are pinned at the perimeter, and support an equilateral triangle of B-type boundaries at the centre. The A- and B-type boundaries meet at \( B_{150}A_{150}B_{60}B \) vertices.

If the distance between the corners of the fixed perimeter vertices is \( l \) and the lengths of the A- and B-type segments are \( a \) and \( b \) respectively then the relationship between the three is

\[
l = \sqrt{3}a + b. \tag{11.12}
\]

If the line energy of the segments is \( \lambda_i \) for the A-type segments and \( \sigma_i \) for the B-type segments then the total energy is

\[
E = a \sum_{i=1}^{3} \lambda_i + b \sum_{i=1}^{3} \sigma_i. \tag{11.13}
\]

Assume for a moment that all the line energies are the same (i.e. \( \sigma_i = \lambda_j \) for all \( i \) and \( j \)). In this case the energy is minimized by minimizing the total segment length so \( a = l \), \( b = 0 \), and the interior domain shrinks to nothing, as shown by Fig. 11.11c. With the destruction of the central cell, the number of sides for the remaining cells decreases by one. In foam physics this known as a T2. There, the surface tension of
all edges is the same [201]. Thus, three sided cells always shrink and disappear. In fact, for foams the only thing stopping the decay under the force of surface tension is the internal pressure, and the slowness of diffusion through the cell wall.

For reconstruction domains however, there is no pressure, and the line tension of the boundary depends upon its character (i.e. the shift and the propagation direction). So the evolution will not be dictated by boundary length arguments alone. For example if \( \sum \lambda_i > \sqrt{3} \sum \sigma_i \) then the energy balance will favour B-type boundaries and the system will evolve towards Fig. 11.11a \( (a = 0, \text{ and } b = l) \), even from the state in 11.11c at the other extreme. We call this process inverse-T\( _2 \) or T\( _2^{-1} \). Note that \( \sqrt{3} \sim 1.7 \) so this process requires a significant energy advantage of the A-type segments over the B-type ones to be favourable. The kinetics of this process — e.g. what sort of nucleation is necessary, how big a barrier exists — are also unknown. However, it does demonstrate a mechanism whereby a new domain could be created, where one previously did not exist.

![Figure 11.11: The T2 Process.](image)

The triangular domain in the centre panel can shrink and disappear. This is called a T2 process. However, if the boundary energy of the dotted lines is less than the solid ones then the central domain can instead grow, an inverse-T2 process.
11.6.3 Dissociation

In introducing the notation used for vertices it was mentioned that it could be applied to vertices whose boundaries were parallel. This section examines just such a case: $X_{180} X_{180} X_0 X$. An example of this is shown in Fig. 11.12. On the left is a single boundary $X[pq]$, on the right there are two $X[nm]$, and $X[rs]$. All three boundaries are of the same type, and the results are valid for boundaries of either type.

This is one of the few cases where the arithmetic is as simple in standard representation as it would be when using ordinary shift vectors

$$p = n + r$$

$$q = m + s.$$  \hspace{1cm} (11.14) \hspace{1cm} (11.15)

If the energy of the single boundary is $\lambda_o$ and the energies of the other two are $\lambda_1$
and $\lambda_2$ then the energies per unit length on the right and left sides of the vertex are

$$E_\leftarrow = \lambda_o$$

$$E_\rightarrow = \lambda_1 + \lambda_2.$$  \hspace{1cm} (11.16)

If $E_\leftarrow < E_\rightarrow$ then the single boundary is favoured. In this case the two parallel boundaries that meet will recombine into a single one and the vertex will move to the right. On the other hand if the opposite is true, and the sum of the boundary energies on the right is less than the energy on the left, then the boundary will evolve towards the left and a new domain will be formed. The single boundary will dissociate into two. For any single boundary, there are 23 different pairs (24 combinations less the one that results in itself plus a X[00] non-boundary) into which it can dissociate.

The incidence of parallel B[\overline{2}2] boundaries is high. Figure 11.13 shows some examples. These may be the result of the following dissociation reaction:

$$B[1\overline{1}] \rightarrow 2B[\overline{2}2].$$  \hspace{1cm} (11.18)

But B[1\overline{1}] itself can be composed of two indirect A-type paths, in fact a pair of enantiomers

$$A[\overline{1}0] + A[0\overline{1}] \rightarrow B[1\overline{1}] \rightarrow 2B[\overline{2}2].$$  \hspace{1cm} (11.19)

Examination of the histograms in Sec. 11.1 shows that A[\overline{1}0] and A[0\overline{1}] have very low abundances — taken together they have the lowest frequency of any A-type pair. This process suggests why that might be: the two high-energy A-type boundaries, or the single high-energy B-type boundary, can be replaced with a pair of low-energy B[\overline{2}2] boundaries.
Figure 11.13: Parallel B$[\bar{2} \bar{2}]$ Boundaries. Some examples of nearby B$[\bar{2} \bar{2}]$ boundaries, possibly the products of dissociation.
Figure 11.14: Domain Boundary Annihilation. Two boundaries glide towards one another. If their characters and relative angles are correct, when they meet they will cancel one another. The result is a high-angle kinks and the merging of two domains.

Annihilation

If $X[nm]=X[−r−s]$ then $p = q = 0$ — if two boundaries are the inverse of one another and they come together in parallel they will annihilate one another. In this case the single non-boundary is always preferred to the double boundary since it’s line energy is $\lambda_o = 0$, while for real boundaries it is always $> 0$. Annihilation has no corresponding phenomenon in foam physics.

Annihilation is not limited to the meeting of parallel boundaries. Figure 11.14 shows a T1-like process where two vertices glide towards one another. When they meet, instead of forming a short segment between them, the two vertices split into two kinks separated by a gap. The condition for this happening is that boundaries 2 and 3 be related to one another by a kink, or, said another way, that boundaries 1 and 4 must have the same character. Once the gap opens the high-angle kinks that remain will rapidly recede since they are now unsupported.
Figure 11.15: Collective Glide. By moving from its original position (dashed line) to one with a shorter length a boundary lowers its energy. However, the barrier to moving the entire boundary collectively scales with the boundary length.

11.7 Kinetics

So far, these processes have been discussed from a thermodynamic perspective, by comparing energies of different domain boundary configurations with little regard for the pathway between those configurations. This section briefly outlines some of the effects that are expected to influence the kinetics of domain boundary evolution.

11.7.1 Changes in Atomic Density

The first factor is the different atom density in each domain boundary. This requires a source or sink of atoms if one boundary is to transform into another. At even moderate temperatures the adatom mobility of Ge is high [37], so the surface can be assumed to be a good reservoir of adatoms for incorporation into or removal from boundaries in flux.
11.7.2 Barrier to Lateral Motion

Collective Glide

Imagine a long boundary of length $l$ which displaces perpendicularly to its direction of propagation by a distance $d$. Since the surface is periodic there is a shortest distance $d$ which the boundary, when displaced by, returns to an equivalent symmetric position. For an A-type boundary on $5 \times 5$ the minimum shift is $5\sqrt{3}/2a_o$ and for a B-type boundary $5/2a_o$. The line energy per unit length is the same before and after the displacement, but there is a barrier $E_B$ per unit length that must be overcome. The boundary glides between two other boundaries at its ends such that after the displacement it is shorter. For the sake of argument assume that any changes to the surrounding boundaries are energy neutral. If that is the case then the decrease in the central boundary makes the process energetically favourable. The magnitude and profile of this barrier will depend in a complicated way on the manner in which the atomic bonds are broken to shift atoms from one side of the boundary to the other. It is not clear that the height of the barrier $E_B$ has any relationship to the energy of the barrier $\lambda$ (i.e. low energy boundaries may have high barriers to glide). It is certain, however, that the a barrier does exist since boundary diffusion does not occur at room temperature. Since the barrier energy is an extensive property the barrier to the entire boundary displacing simultaneously grows proportionally with boundary length. Thus, collective glide is very unlikely. In general, boundaries are expected to move laterally in units of the smallest possible segments, which are $T_A$ and $T_B$.

Essentially this is the same argument that forbids erasure of a domain boundary through collective glide of the entire domain. In that case the kinetic barrier scales
with the area of the domain (2D), in the case of boundary glide it scales with length of the boundary (1D), and in sequential glide the barrier is a constant (0D).

**Sequential Displacement**

Figure. 11.16 shows the glide of a boundary by sequential displacement. The initial and final states are the same as those in the previous section. However, the path taken between involves incremental changes to the boundary. It starts in frame II with the formation of a kink and a small segment labeled \( s_2 \). Later, a similar segment \( s_3 \) forms at the other end of the boundary. Since only a small segment moves at a time the kinetic barrier to movement of the kink is relatively small. However, since \( s_1 \) and \( s_2 \) have different characters (unless they are enantiomorphs) they can be expected to possess not only different line energies \( \lambda \) but also face different barriers to diffusion. Therefore the different ends of the “bulge” that forms will have different mobilities. In practice, the differences in mobility and surface energy mean that one will likely dominate over the other.

At one of the intermediate steps the total energy is

\[
E = (l - 2\sqrt{3}d)\lambda_1 + 2d(\lambda_2 + \lambda_3). \tag{11.20}
\]

If \( \lambda_2 + \lambda_3 > \sqrt{3}\lambda_1 \) then there is an energetic barrier to introducing the extra segments necessary to move sequentially from the initial to final configuration. As discussed earlier, the displacement \( d \) cannot be infinitesimally small, so the barrier (if indeed the energy is positive) is always finite. So, sequential displacement introduces another kinetic barrier apart from that due to segment glide. An example of an \( A[20] \) boundary in the process of sequential displacement is shown in Fig. 11.16c. In this
**Figure 11.16: Glide by Successive Displacement.** The boundary moves by displacing one small segment at a time until it has moved from the initial trajectory (dashed line) to the product, a shorter path. A schematic of the reaction energy is shown on the right. c and d) Examples of boundaries in the process of sequential displacement. The arrow show pairs of kinks that act in opposite senses.
case the lower segment is B[22] and the upper one is A[22]. Figure 11.16d shows another example with B[22] under displacement. Examples like these, where two pairs of nearby kinks act in opposite senses, are very rare especially among preferred boundaries like these.

One point to make is that while we have been viewing the boundary sections $s_2$ and $s_3$ as short segments of a longer translationally invariant boundary, in reality, since $d$ is on the order of the size of a unit cell, the entire kink structure is perhaps better regarded as an entity of its own.

Finally, for the entire existence of the bulge (between III and IV on the reaction diagram), there is no energetic preference to incremental changes in its length in either direction. So there is not a continuous thermodynamic drive from the initial state to the final one. In other words there is no pressure and the lateral motion of the boundary is a process of diffusion.

11.8 Summary

The distribution of domain boundary characters is not uniform, but shows strong preference for boundaries in the orbit [20]. The boundary B[22] in fact makes up almost half of all boundaries by length. The peaks in the distribution are taken as reflective of lower line energies for the preferred boundaries. The ultimate reason for the various line energies must lie in the details of the atomic structure, for which further insight awaits calculations. However, some model processes by which the network of boundaries might evolve from an initially uniform distribution of characters to the one observed are presented. They include kinking, the T1 and T2 processes familiar from foam physics, and annihilation. The basis of all of them is that by
changing the character of a boundary, through kinking or the motion of a vertex, the total energy of the boundary network can be reduced even if the total path length is increased. A very brief discussion was presented some of the kinetic limitations that might exist to free boundary movement.
Chapter 12

Cluster Growth on Ge DAS Surfaces

Having seen the effectiveness of $7\times7$ in confining and organizing the Group 13 magic clusters it is natural to ask whether the same principle can be applied to different DAS reconstructions to allow a range of magic cluster sizes determined by the surface reconstruction size. In short, can the family of DAS reconstructions be used as an effective template for Group 13 magic cluster growth?

12.1 Earlier Work

Work on this question was begun by Jenny MacLeod [116, 115]. Samples were prepared by first growing a $\sim 1.5$ BL thick wetting layer of Ge on Si(111). Then In was deposited in the same manner used to grow magic clusters on Si(111)$7\times7$: a deposition rate of $\sim 0.15$ ML/min onto the substrate held at $\sim 150^\circ$C. The results for In coverage of 0.06, 0.011, and 0.023 ML are shown in Fig. 12.1. Unlike $7\times7$, where
Figure 12.1: In clusters on $5 \times 5$. The observed features can be described as i) single HUC clusters, ii) double HUC clusters, iii) four HUC clusters, iv) dark UHUCs, and v) streaked FHUCs. The populations of each feature varies with coverage: a) 0.06, b) 0.11, to c) 0.23 ML. Area $30 \times 30 \text{nm}^2$, $V = -1.50 \text{V}$. Image reprinted from Ref. [116] with permission from the American Physical Society.
clusters are monodispersed, there are a several different features on 5×5 described as i) single HUC clusters (1HUC), ii) double HUC clusters (2HUC), iii) four HUC clusters (4HUC) iv) dark UHUCs and v) streaked FHUCs. The individual 1HUC clusters are mostly found within the FHUC. The 2HUC clusters include a faulted and unfaulted HUC and cover the dimer boundary which divide the halves. The 4HUC clusters span three FHUCs and the UHUC between them. The forms for each of these cluster types is highly variable. The streaked HUCs are always in the FHUC, and their appearance is consistent with rapidly diffusing adatoms trapped within a HUC [162, 209]. The frequency of these observed features are listed in Table 12.1.

The accompanying \textit{ab initio} calculations illustrate that for individual In adatoms the preferred bonding site, with bonding energy \(\sim-2.8\) eV, is at the \(H_3\) site near the 5×5 restatom. Several adjacent high symmetry sites (\(B_2\), and \(T_4\)) also have low energies, so a basin of attraction like the one proposed by Cho and Kaxiras [38] is found around the restatom. The barrier to diffusion around the basin is 0.15-0.35 eV in the UHUC and 0.36-0.42 eV for the FHUC. The energy barrier to diffusion between HUCs was found to be very large. The absolute minimum energy configuration for an individual In adatom is in at \(H_3\) in the FHUC. The assymetry between faulted and unfaulted halves is \(\sim0.15\). This is consistant with the observed frequency of clustering and streaking in the STM images.

Further calculations were performed to explore the effect of increasing the In content [147]. For both 2 and 3 In atoms per HUC the preferred bonding sites are at \(H_3\), with each In atom occupying its own site. However, neither of these configurations have an energy lower than that of isolated In adatoms in separate HUCs. This suggests that In atoms will remain isolated until the coverage is high.
Table 12.1: In Cluster on 5×5 Statistics. The relative abundances of each of the features shown in Fig. 12.1 are listed as a function of In coverage. Adapted from Ref. [113].

<table>
<thead>
<tr>
<th>Feature</th>
<th>0.06 ML</th>
<th>0.11 ML</th>
<th>0.23 ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) 1HUC - FHUC</td>
<td>17%</td>
<td>18%</td>
<td>25%</td>
</tr>
<tr>
<td>- UHUC</td>
<td>1</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>ii) 2HUC</td>
<td>14</td>
<td>18</td>
<td>28</td>
</tr>
<tr>
<td>iii) 4HUC</td>
<td>7</td>
<td>14</td>
<td>22</td>
</tr>
<tr>
<td>iv) Dark FHUC</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>v) Streaked FHUC</td>
<td>36</td>
<td>44</td>
<td>15</td>
</tr>
<tr>
<td>Empty - FHUC</td>
<td>26</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>- UHUC</td>
<td>80</td>
<td>70</td>
<td>60</td>
</tr>
</tbody>
</table>

enough to force multiple occupation. This is clearly at odds with the STM results which show cluster coexisting with bare 5×5. So far, there have been no ab initio studies of more complex cluster geometries on 5×5.

12.2 Ga on 5×5

On Si(111)7×7, Ga forms magic clusters. When a Ga coverage of 0.07 ML is deposited on 5×5 at a temperature of ~100°C it forms a variety of different cluster features. The observed features can be grouped roughly into types i & ii: single HUC and 2HUC clusters respectively. As with In, the single HUC features adopt a variety of shapes, some triangular and symmetric and others elongated. The HUC preference of the 1HUC features is roughly 3:1, much less than the 17:1 observed for In clusters at this coverage. The 2HUC clusters are an symmetric hourglass centred on a dimer line dividing two HUCs. Their appearance is more consistent than the 1HUC ones. Aside from these two types of features there are others that are more difficult to categorize, including irregular multi-HUC structures, which may be related to the 4HUC features seen with In, and features which cover corner holes.
Figure 12.2: Ga Clusters on 5×5. a) With 0.05 ML of Ga. The darkened strips cover domain boundaries where the 5×5 periodicity is broken. Observed features follow those seen for In (Fig. 12.1): i) single HUC clusters, and ii) 2HUC clusters. Image parameters: a) $V=2.2\, V$, $100\times45\, \text{nm}^2$, b) $V=2.1\, V$, $35\times20\, \text{nm}^2$. 
12.3 Structure of Clusters on 5 × 5

Despite its similarities, it seems that 5×5 does not support magic clusters of the type seen on 7×7. Why this is can be seen by considering the clusters of Ga that form on Si(111)-Ga√3×√3.

12.3.1 Ga Random Clusters

Ga on Si(111)-Ga√3×√3 forms triangular magic clusters of a variety of sizes (cf. Section 6.1), which are called Ga random clusters after Ref. [200, 98]. For large clusters the internal atomic arrangement is similar to graphene, with alternating Ga and Si atoms. The stoichiometry of a cluster with \( n \) Ga atoms along one edge is \( \text{Ga}_{\frac{n}{2}}\text{Si}_{\frac{n}{2}} \). The Group 13 magic clusters that form on 7×7, have the same structure as the \( n = 3 \) version of these random clusters: \( \text{Me}_6\text{Si}_3 \), where Me is one of Al, Ga, or In. This is the largest cluster that will fit within the 7×7 HUC. For an arbitrary DAS \( N \times N \) unit cell, the largest Ga random cluster that will fit within the a HUC has size \( n = \frac{1}{2}(N - 1) \). Figure 12.3 shows such hypothetical constrained clusters. The accompanying table provides statistics on the number of substrate dangling bonds saturated by each configuration, and the change in the number of substrate atoms necessary to form each cluster.

Comparing the cases for 5×5 and 7×7 (Figs. 12.3a & b) two things become apparent: first, the tremendous dangling bond reduction that comes from magic cluster formation on 7×7 is absent on 5×5; second forming a \( \text{Me}_3\text{Ge} \) cluster on 5×5 requires that two adatoms be ejected from the HUC, on the other hand for a \( \text{Me}_6\text{Ge}_{13} \) cluster on 7×7 the Si stoichiometry remains unchanged. These two factors — one thermodynamic, one kinetic — illustrate why the Group 13 clusters on 7×7 are so
Figure 12.3: Constrained Random Clusters. The largest Ga-type random clusters that will fit within a unit cell of DAS a) 5×5, b) 7×7, c) 9×9, and d) 11×11. The table provides statistics on the number of metal atoms (# Me), change in the number of Ge atoms (ΔGe) and dangling bond reduction (ΔDB) that accompanies the formation of each cluster. Also shown are alternative forms for e) 9×9 and f) 11×11 using smaller than maximal clusters. Condensing the cell in f by removing the grey area results in Fig. 12.6. Colour scheme follows that of Figs 3.4 and 6.3.
easily formed, and why on 5×5 clusters, at least of this type, are not.

As an exercise, the maximally sized random clusters in the 9×9 and 11×11 reconstructions are shown in Figs. 12.3c & d. Both demand changes to the count of Ge atoms in the HUC, and neither matches the reduction in dangling bond density achieved by the Me₆Ge₃ clusters on 7×7. Figures 12.3e & f show the same reconstructions with multiple smaller random clusters. For 9×9, three Me₃Ge rather than a single Me₁₀Ge₆ cluster greatly reduces the number of dangling bonds, but adds two extra Ge atoms to be disposed of. Interestingly, on 11×11 three Me₆Ge₃ clusters also results in greater dangling bond saturation, but contains the same number of Ge atoms as the clean reconstruction. The discussion of the larger reconstructions is largely academic since they cannot be grown in practice over large areas with good order. However the 3×Me₆Ge₃ configuration for 11×11 is suggestive of the 4HUC clusters seen on 5×5, which will be explored further in Sec. 12.3.3.

12.3.2 2HUC Features - Hourglass

What can be said about the structure of the clusters that do form with In and Ga exposure on 5×5? Two features found in Fig. 12.1 will be considered in greater detail. The 4HUC clusters will be examined in Sec. 12.3.3 and the 2HUC clusters here. Figure 12.4a shows 2HUC clusters in empty state images, where they have the appearance of an hourglass straddling the dimer line. Under optimal growth conditions these clusters can be made more uniform than the other features, but there is still some variance in their appearance. The clusters are found in three distinct orientations, differing by 120°. The tallest part of the cluster, which lies at the centre of the UC, is ~1.3 Å higher than the adjacent adatom peaks. This is somewhat larger
than the 1.1 Å height of In magic clusters on 7×7. There are shoulders on the peak ~15 Å wide when viewed along the long diagonal of the unit cell.

In filled state images (Fig. 12.5), the clusters appear more square over the dimer row, but there is a distinct asymmetry between the exposed corner adatoms in the faulted vs unfaulted halves. In filled state images the clusters appear as large featureless blobs that fill the rectangular area between the four adjacent corner adatoms. The two distinct adatoms at opposite ends of the unit cell both appear brighter than normal, the one in the FHUC particularly so.

Figure 12.5 shows a proposed structure for the 2HUC cluster. Three In adatoms in each HUC support two displaced Si adatoms which dimerise with a partner in the opposite HUC. The adatoms at opposite ends of the UC are unperturbed. This configuration requires the addition of six In adatoms, but contains the same number of Si adatoms as the original 5×5 reconstruction. There is no rearrangement of atoms in the restlayer and lower; like the magic clusters on 7×7 all the changes happen in the adatom layer. This arrangement reduces the number of dangling bonds to only the two on the remaining adatoms. Unfortunately, DFT calculations do not support this as a thermodynamically stable configuration [146]. The calculated binding energy per In atom is 2.07 eV (with GGA), less than the binding energy for an individual In atom, 2.27 eV [146]. So, once again, calculations predict that In atoms should disperse to singly occupy HUCs, and multi-In clusters should only appear after all HUCs are filled.
Figure 12.4: The 2HUC Clusters. The arrow indicates a 4HUC cluster, which resembles three coalesced 2HUC clusters. The In coverage is 0.05 ML.
12.3.3 4HUC Features

The second features of interest are the 4HUCs, shown in detail in Fig. 12.6a. These cover three FHUCs surrounding a single UHUC. In filled state images they have a tall, irregular, and lumpy appearance at the center of the cluster. However the three adatoms in the distant corners remain distinct. In empty states they look more uniform and resemble three 2HUC hourglasses arranged around the perimeter of the central UHUC. Two possible atomic structures for these features are discussed. In light of their large unit cell, complementary calculations are not possible, but two different starting points will be considered: the dimer bridges proposed for the 2HUC (Fig. 12.5c), and the Me₆Ge₃ clusters found on 7×7 (Fig. 12.3b).

The hypothetical 2HUC structure shown in Fig. 12.5c can be multiplied to cover
four HUCs in the manner shown in Fig. 12.6b. The three metal adatoms in the FHUCs are bonded in the same way as isolated 2HUC. In three metal edge adatoms in the UHUC are also bonded in the same way. However, the three corner metal atoms are coordinated to the restlayer below and \textit{two} Ge adatoms which bridge to different adjacent FHUCs. The weak links in the structure are the large dihedral angle demanded of these corner metal atoms and the long Ge bridging bond over the dimer row. It also requires the influx of four Si atoms in addition to the 15 metal atoms. On the other hand this structure is consistent with the superficial resemblance between the 2HUC and 4HUC clusters, especially in empty state images. It also satisfies all of the unsaturated bonds in the 4HUC reducing 18 dangling bonds to 5 (3 corner adatoms and 2 corner holes). It does this without any substrate rearrangement.

In Sec. 12.3 the analysis included discussion of 9×9 and 11×11 DAS unit cells. Although these are not practical, the 3×Me₆Ge₃ configuration for 11×11 is suggestive of the 4HUC clusters seen on 5×5. If the stacking sequence in the central UHUC of four 5×5 HUCs is changed so that it is also faulted, a new triangular cell of size 10×10, shown schematically in Fig. 12.6c and d, is formed. Moreover, the cluster structure shown in Fig. 12.3f can be condensed to fit within a 10×10 cell by removing the shaded region from the centre. The result is shown in Fig. 12.6b. As drawn, the three central restlayer atoms are overcoordinated, bonded to five adjacent atoms (three dimer layer atoms, and two metal atoms), so the model is surely wrong in detail. It is also at odds with the fact that the UHUC is energetically preferred to the FHUC. All other things being equal it would be better to remove the stacking fault in the a FHUC rather than introducing one in an UHUC. The final objection is that at the growth temperature there ought not to be enough thermal energy to reverse the stacking fault. However,
Figure 12.6: 4HUC Structure. a) A selection of 4HUC clusters as seen in filled and empty states. b) A possible structure for such clusters composed of three 2HUC clusters (Fig. 12.5). c) An alternative structure for such clusters based on three \( \text{Me}_6\text{Ge}_3 \) merged within a 10\( \times \) area. d) To achieve this configuration, the central UHUC must switch stacking creating a 10\( \times \) triangle with faulted stacking.
it agrees with the STM images in three respects. First, the three corner adatoms in
the 4HUC corners are distinct, and display enhanced contrast as they do for Me$_6$Si$_3$
clusters. Second, the observed height is slightly lower at the 4HUC centre, where
the model shows reduced metal density, than towards the corners, where the merged
clusters have their centres. Finally, the variation in observed morphology is consistent
with different modes for resolving the overcoordination of the three central restlayer
atoms.

12.4 Clusters on Ge7×7

Clearly, the clusters that form on Ge5×5 are more poorly defined than those which
form on Si7×7. This could arise for two distinct reasons: because the substrate is
Ge (or more precisely a Ge/Si mixture) or because of the different reconstructions.
The multiphase surfaces introduced in Sec. 5.6 provide a surface with both high
Ge-content 7×7 and 5×5 in immediate proximity.

Multiphase surfaces prepared by low temperature SPE in the manner explained in
Sec. 5.6 were exposed to In and Ga at 150°C. Images of the results for In (0.6 ML) and
Ga (0.7 ML) are shown in Figs. 12.7 and 12.8. In both cases magic clusters appear on
both the substrate and island 7×7 domains. However, there is very little adsorbate
found on the island 5×5 domains. In the case of In the 5×5 is virtually bare, although
there is some Ga there in the form 1HUC and 2HUC features. With increasing In
coverage, shown in Fig. 12.9, this pattern persists. Even when the domains of 7×7
are more than half-covered (Fig. 12.9c) clusters form in the 7×7 UHUC and leave
the 5×5 uncovered. It is not until the domains of 7×7 are fully-covered (12.9d) that
In starts to appear on the 5×5.
Figure 12.7: In Magic Clusters on Multiphase Ge. The islands, standing above the 7×7 substrate, contain domains of 5×5 and 7×7. The In clusters segregate to the 7×7 areas and leave the 5×5 areas bare. The same two clusters have been highlighted in both images. In coverage is 0.06 ML. Image areas are 75×40 nm².

Figure 12.8: Ga Magic Clusters on Multiphase Ge. Ga coverage is 0.7 ML. Magic cluster formation is again restricted to domains of 7×7.
Figure 12.9: Coverage Dependence of In Magic Clusters on Multiphase Ge. In coverages of a) 0.02, b) 0.06, c) 0.12, d) 0.22 ML. Right up to half coverage (0.125 ML) the In magic clusters are found only on the 7×7 domains. Image areas 100×100 nm. All images at +1.5 V except b at 2.0 V.
The chemical makeup of the islands and the substrate on which they sit is unknown. It could be that the exposed substrate remains pure Si and the islands are entirely Ge. However it is likely that they are both of mixed species, and the intermixing could be as high as 50% [24, 154]. In either event the results show that clustering on $7\times7$ is not inhibited by Ge in the unit cell. So the absence of In on Ge$5\times5$ is not due to chemical reasons, but instead structural ones. This effect is not unprecedented: Cherepanov et al. observed that for Si and Ge adsorbed on multiphase Ge surfaces, clusters were found only on the $7\times7$ domains [37].

On the relaxed Ge$7\times7$, found on top of tall 3D islands, In shows the same behavior. Figure 12.10 shows 3D Ge islands grown by SPE with 7.5 BL of Ge annealed at 575°C for 7 min. The surface was then exposed to 0.10 ML of In at 150°C. Indium magic clusters form on the relaxed islands that have $7\times7$ reconstruction.
12.5 Summary

In this chapter the behaviour of In and Ga was investigated on the Ge5×5 and Ge7×7 reconstructions. In short, both these adsorbates, which form magic clusters on 7×7, do cluster, but not magically, on 5×5. Several types of clusters dominate, although they are irregular in appearance. The lack of magic clustering on 5×5 was explained by reference to the structure of Ga random clusters. Clusters having that structure but confined to unit cells of the DAS reconstruction are particularly, based on dangling bond reduction and changes in local stoichiometry, for 7×7, but not 5×5. Interestingly, hypothetical models for the larger DAS unit cells suggest higher stability for 11×11. Models for the irregular 2HUC and 4HUC structures were presented. In the first case the model is not supported by DFT calculations. In the latter, the large cell makes DFT calculations infeasible. That the lack of magic clustering on Ge5×5 is due to structural differences with Si7×7 rather than chemical ones was verified by observing cluster growth on multiphase surfaces. On these surfaces In and Ga form magic clusters on the domains of 7×7, both on the substrate and 1 BL islands, even though they are Ge rich. On the other hand, no clustering, and little adhesion was observed for the adsorbates on the domains of 5×5. This was reinforced by the observation of magic clusters on tall relaxed islands of Ge7×7.
Chapter 13

Clusters on Domain Boundaries

Having shown that magic clusters form on 7×7, but not on 5×5 and having explored the atomic structure, and interactions of domain boundaries of 5×5, this chapter turns to demonstrating the utility of domain boundaries for patterning magic clusters.

13.1 Preparation

The behaviour of In and Ga was examined after deposition on Ge5×5 surfaces, prepared in the manner described in Sec. 5.6, to generate high densities of domain boundaries. The metal adsorbates were deposited onto a substrate held at \( \sim 100^\circ \) C and annealed for 2 min afterwards. Indium deposition rates were 0.028 ML/min and Ga 0.005 ML/min, as measured by a thickness monitor. The total nominal coverage, based on previously measured rate and exposure time, ranged from 0.025–0.14 ML.
Figure 13.1: Ga Clusters at DB. Bright features indicate clusters of Ga. They are concentrated at the domain boundaries, particularly B[2 2]. However, some boundaries remain uncovered. The large image is $75 \times 75 \text{nm}^2$. Nominal Ga coverage is 0.025 ML; $V=+1.5 \text{V}$.
In Ga 8042 fi37 8165 FD28 +2.5V 
U F U F +1.5V A[02] B[22]

Figure 13.2: In and Ga Magic Clusters on B[22]. Nominal coverage and bias voltages are: In: 0.083 ML, +1.5 V; Ga: 0.025 ML, +2.5 V.

13.2 Results

Figure 13.1 encapsulates the experimental results. It shows a terrace of Ge5×5 threaded by a variety of domain boundaries. The bright protrusions are taken to be Ga clusters. There are several that appear within the domains, but the majority of clusters are found at the domain boundaries. The largest distance from the domain interior to its boundary is \( \sim 25 \text{ nm} \), suggesting a diffusion length of this scale. The B[22] and B[22] boundaries are densely covered, whereas the A[22], A[20] boundaries are largely bare. On the B[22] boundary the clusters are especially regular and, on closer inspection, as shown in Fig. 13.2, closely resemble the Group 13 clusters found on 7×7.
13.3 Clusters on B[\bar{2}2]

Filled and empty state images of In clusters on B[\bar{2}2] can be seen in Fig. 13.3. The empty state images show that the clusters have an equilateral triangle shape with a shallow depression in the centre. This triangle can be resolved into six protrusions; the three at the corners being slightly dimmer than the three along the edges. The cluster is positioned in the faulted half of what would be the centre of a complete 7×7 unit cell. However, since the boundary unit cell is truncated, the corner hole encroaches on the cluster. In the filled state images the cluster itself is less prominent and it appears as a small compact oval at the same position as the empty state image. The two Si corner adatoms in the same HUC appear brighter suggesting charge transfer.

The appearance of the Ga cluster is slightly different, as seen in Fig. 13.4. In this case, at low empty biases (top row of Fig. 13.4) the cluster instead appears as a triangle of three atoms positioned in the FHUC. As the bias increases these three edge atoms becomes less distinct and the corner atoms of the cluster grow brighter resulting in the familiar triangular shape (Fig. 13.2b shows a better image

**Figure 13.3: STM Images of B[\bar{2}2] In Clusters.** The unit cell outline encloses the same cell in both the filled (left) and empty (right) state images. Note the absence of clusters on the adjoining A[02] segment.
Figure 13.4: STM Images of B[22] Ga Clusters. The top images show empty states, the bottom filled states. Most of the clusters fall on the FHUC of the B[22] boundaries. The arrows indicate the few clusters in UHUCs. Again, note the absence of clusters on the A[02] segments. Images are 25×40 nm².
of Ga clusters at high bias). At low filled state biases (-1.5 V) clusters appear as depressions with intensity lower that that found in empty B[122] cells. Again, the two corner Si adatoms in the HUC appear brighter. As the bias is increased (i.e. becomes more negative) the size and intensity of the cluster grows until at -2.5 V it has become very bright.

At low coverages most of the clusters form in the FHUC, however several UHUC clusters can be seen in Fig. 13.4 and indicated with arrows. At low positive bias (+1.5 V) these differ in appearance from their FHUC counterparts by being dimmer. That difference has disappeared by +1.8 V. At all negative biases this is repeated and UHUC clusters appear less tall than FHUC ones. At the lowest bias (-1.5 V) they appear as depressions almost as deep as the adjacent boundary hole. Another important difference is that there is no enhancement to the apparent height of the two Si corner adatoms.

In all respects the clusters of In and Ga observed on B[122] boundaries appear identical to the ones found on 7×7. A proposed structure is found in Fig. 13.5. It is

Figure 13.5: Structure of B[122] clusters. The model is an amalgamation of the quasi-7×7 structure of B[122] (Fig. 9.23) combined with a Group 13 cluster (Fig. 6.3).
a simple combination of the model for B[2 2] and a Group 13 cluster. The important difference from clusters on 7×7 (Fig. 6.3) is the absence of the third Si adatom and the proximity to the large boundary hole. This model does not alleviate the difficulty of the large number of dangling bonds present in the boundary hole. However, it does reduce the number of Ge dangling bonds from 23 to 17.

13.3.1 HUC Preference

A number of factors make a coverage dependance survey of clusters difficult. The first is that there are large uncertainties associated with the nominal coverage measured by the thickness monitor for the very small overlayers used here. More importantly, this is magnified by the fact that domain boundary density varies over the surface. Since the metal adsorbate predominantly segregates to the domain boundaries, the 1D adsorbate density at domain boundaries is very sensitive to uncertainty in the original 2D coverage and the 2D density of domain boundaries in the vicinity. To overcome this problem the cluster number density \( \phi \) was calculated as the number of clusters per B[2 2] unit cell. Half coverage corresponds to 1 cluster per unit cell, full coverage to 2. Figure 13.6 shows examples of In B[2 2] clusters at nominal coverages of 0.056, 0.084, and 0.14 ML which correspond to \( \phi = 0.69, 1.39 \) and 2.0 clusters/B[2 2] UC.

At low coverages the clusters fall predominantly in the FHUC, once all of those are full, the surface is half-covered, clusters appear in the UHUC until finally all HUCs are full and the boundary is saturated. The preference \( P \) can be calculated as

\[
P = \frac{f/F}{f/F + u/U},
\]  

(13.1)
Figure 13.6: In B[22] Cluster Coverage Dependence. STM images of In clusters on B[22] at coverages of 0.69, 1.39 and 2.0 clusters/B[22] unit cell.
Figure 13.7: The F/UHUC Preference of B[22] Clusters. The results for Ga (open triangles), and In (closed squares) for B[22] clusters are superimposed upon the data for clusters on Si(111)7×7 (faded, adapted from Fig. 6.4). The behaviour of both adsorbates follows the trend for In on 7×7 which is markedly different than that of Ga.
where $U$ and $F$ are the number of FHUCs and UHUCs, and $u$ and $f$ are the number of clusters found in FHUCs and UHUCs. This definition has been modified from that introduced in Ch. 6 to accommodate the slight differences between the number of faulted and unfaulted $B[\bar{2}2]$ HUCs that arise from kinks and vertices.

The results are summarized in Fig. 13.7 which shows the data for $B[22]$ boundaries superimposed upon those for $7\times7$ clusters (Fig. 6.4). Both the In and Ga results closely follow the trendline for In magic clusters on $7\times7$ previously published in Ref. [200]. For boundary clusters the FHUC is strongly preferred for cluster formation right up to half-coverage. For Ga this is markedly different from the $7\times7$ substrate. In that case, Ga clusters show a FHUC preference only at the lowest densities. This indicates that the energy difference between F/UHUC occupation is closer to that for In on Si(111)$7\times7$ than for Ga. The difference in behaviour could be attributed to several factors: the mixed Ge/Si substrate, the truncated unit cell, or the presence of a high mobility channel in the form of the adjacent $5\times5$ domains.

### 13.4 Clustering on $A[02]/A[20]$

As seen in Figs. 13.2, 13.3, and 13.4 magic clusters do not, at low coverages, form on the $A[02]/A[20]$ boundary, despite cluster formation on adjacent sections of $B[22]$, and the fact that the unit cell for these boundaries is also a truncated $7\times7$ HUC (see 9). However, for both $A[02]$ and $A[20]$ that unit cell is an unfaulted HUC. Since there is a strong preference for FHUC cluster formation, the absence of clusters at low coverages on $A[02]/A[20]$ is unsurprising.

Figure 13.8 shows an example of three magic clusters on the unfaulted halves of an $A[02]$ boundary and a fourth on the kink core that links that segment to the adjacent
Figure 13.8: Ga Magic Clusters on A[0 2]. At a coverage of $\phi = 1.55$ there is significant filling of the UHUCs, in this case of A[0 2].

At a coverage of $\phi = 1.55$ there is significant filling of the UHUCs, in this case of A[0 2]. In this case the B[2 2] coverage is 1.55 clusters/UC so there is significant filling of the unfaulted quasi-7$\times$7 HUCs, including, as shown, those of A[0 2].

13.5 Other Boundaries

At low coverages, $\phi < 1$, the dominant boundary for cluster formation is B[2 2]. It is certainly the only boundary for which magic clusters are observed. However, other boundaries do capture some adsorbate. Figure 13.9 shows the clusters that form on these other boundaries at a Ge coverage of $\phi = 0.88$. In all cases other than B[2 2] they are irregular, and not magic. There is also a marked difference in the cluster density for different types of boundary. For instance, the A[1 1], A[2 2], A[1 2], A[1 2], A[0 2], and their respective enantiomorphs all appear qualitatively bare. On the other hand A[1 0], B[1 2] and B[2 2] seem densely covered. This sample has an unusually high number of otherwise rare B-type boundaries. It is not clear if this is due to a fluke of statistics, perturbation in preparation routine (particularly Ge annealing
Figure 13.9: Ga Clusters on Other Boundaries. The Ga coverage is $\phi = 0.88$. The character of the minority boundaries have been labeled. For unknown reasons, there are an unusually large number of B-type boundaries present in this sample. There is a clear difference between the cluster density on A[11], for instance, and A[10]. The arrows point to kink sites on A[11] which do have clusters.
Figure 13.10: Domain Boundary Decoration at High Ga Coverage. The total Ga exposure is 0.05 ML, corresponding to $\phi = 1.55$. Again, $A[2\bar{2}]$, $A[0\bar{2}]$, and $A[0\bar{2}]$ are relatively bare.

At higher coverages more metal adsorbate adheres to the domain boundaries, and the number of free clusters within the domain interiors also increases. Figures 13.11 and 13.10 show In and Ga at exposures of 0.05 and 0.14 ML ($\phi = 1.55$ and $\phi = 2$) respectively. In both cases almost all boundaries are now decorated. For instance $A[1\bar{1}]$, which was left bare at $\phi = 0.88$, is overgrown with In in Fig. 13.10b. However there are some boundaries which remain stubbornly exposed: $A[0\bar{2}]$ and $A[0\bar{2}]$ for instance. $A[2\bar{2}]$ seems particularly inert.
Figure 13.11: Domain Boundary Decoration at High In Coverage. The total exposure is 0.14 ML, so the B[22] boundaries, visible in a as bright regular lines, are now entirely saturated ($\phi = 2$). a) A large scale image; the bright lines are domain boundaries covered with In. There is variation in the regularity of the decoration, but almost all boundaries are densely covered with In. The arrows point to boundaries that are unusually bare. b) An A[11] boundary which was uncovered at $\phi = 0.88$, but here is completely saturated. c) shows a relatively bare boundary, A[22].
13.6 Antecedents

The formation of magic clusters on domain boundaries is not wholly without precedent.

We have already mentioned that, in general, domain boundaries are important nucleation sites for adsorbate growth. Experiments conducted at elevated temperatures have shown that mobile Si magic clusters on Si(111) 7×7 are trapped near step edges and domain boundaries [81]. On Si(111)-Ag(√3 × √3) extra Ag adatoms form a 2D adatom gas scattered diffusely within the √3 domain. However, at domain boundaries the adatoms coalesce [162]. The closest parallel to what has been observed here are the Ga random magic clusters that form on Si(111)-Ga(√3 × √3), and were discussed in 6.1 and 12.3. For these, clusters with \( n = 2 \) and \( n = 3 \) form at domain boundaries between √3 domains because these sites allow such clusters to completely eliminate the remaining dangling bonds [199]. The structure of the free \( n = 3 \) cluster corresponds very closely to the magic clusters we observe at the B[22] boundaries. However, the B[22] clusters reported here differ in several important ways: the boundaries are straight and thus so are the arrays of resulting clusters, the clusters are uniform and truly magic, and the domain interiors are comparatively bare. Something similar has been demonstrated using step edges. Recent studies have shown that Si and Ge cluster preferentially at exposed step-edge FHUCs on vicinal Si(111) [165, 166, 167].
13.7 Summary

This section demonstrated that domain boundaries can be used to pattern magic clusters. At low coverages In and Ga diffuse off the domain interiors and onto the domain boundaries. In particular the adsorbates segregate to the B[22] boundaries where the truncated 7×7 unit cell supports the growth of magic clusters of the type found for In and Ga on Si(111)7×7. At higher densities of Ga and In the adsorbates begin to cover the other boundaries. However, even for relatively high coverages several of the boundary types remain bare. The FHUC preference for the B[22] magic clusters is very high, for both In, which is similarly selective on Si(111)7×7, and Ga which is not. Thus, the B[22] uniquely acts as a template for growing straight lines of precisely spaced, atomically identical, nanoscale clusters.
Chapter 14

Conclusions and Future Work

This final chapter proposes several new veins for future investigations and quickly reviews the results of this work.

14.1 Future Work

14.1.1 Single Boundary Growth

Chapter 11 demonstrated that $B_{[\bar{2}2]}$ is the dominant boundary type. In the samples prepared for this study the focus has been on large wide terraces to promote the development of a network of boundaries. If instead, vicinal surfaces were used, boundaries that lay parallel to the step direction would be suppressed because they could be relieved by gliding to either the step edge or root. This would leave only boundaries lying roughly perpendicular to the step which traverse the step from edge to root. In this situation there is no topological restriction to glide, so with sufficient
mobility the boundaries could diffuse up and down the terrace and undergo successive dissociation and recombination reactions which favour the formation of $B[\bar{2}2]$. In fact such a system might be a better choice for measuring the distribution of domain boundary characters precisely because the topological constraints are relaxed.

For Si(111), offcuts in the $[\bar{1}12]$ direction result in straight parallel steps. The B-type boundaries run perpendicular to these steps, as desired. In practice, the trick will be to ensure high domain density in the presence of nearby steps which will act as special nucleation sites and promote ordered growth. This would not work with conventional MBE, but SPE, which has the ability to generate higher domain densities, may make this possible. This is, unfortunately, one of the only ways in which a macroscopic control parameter (surface offcut) might influence the alignment of boundaries. The other control possibility is the direction and nature of the applied heating current.

### 14.1.2 The Need for Calculations

Although models of atomic structure of the domain boundaries have been presented, their structure remains the subject of speculation. The traditional answer to questions of surface structure is to use one of the surface sensitive diffraction techniques (e.g. surface x-ray diffraction, LEED). Unfortunately the boundaries are aperiodic upon the surface and sparsely distributed. Techniques using vicinal surfaces like the one described above might succeed in growing aligned boundaries of a dominant type, but boundary density will always be small compared with the surrounding surface.

Thus, computations are the best hope for verifying the proposed models. Unfortunately, the very large size of the required supercell make ab initio calculations
unfeasible. A minimal supercell consisting of a single B[22] unit cell with adjacent 5×5 one unit cell wide, all extending only three BL deep (including the selvedge layer), contains 768 atoms. So, in the short term \textit{ab initio} methods are not available. However, there are other computational techniques which would be significantly more effective than the primitive bond counting ones demonstrated here, but are still accessible with today’s resources.

14.1.3 Other Reconstructions

As discussed in Ch. 7 shifted domain boundaries are not unique to Si(111)-Ge5×5. It should be possible to devise similar nomenclature for the identification of other boundaries, and for the relationships between boundaries that meet at a vertex. This could even be extended to include boundaries between the other three types of boundaries, between mixed, rotated, and reflected phases. For instance a notation could be devised for boundaries between 7×7 and 5×5. Some interesting possibilities arise. For instance at a boundary between reflected domains, like that seen in Fig. 7.1, the boundary is achiral even though both domains are chiral.

The nomenclature can also be applied to surface steps, and step kinking can be described using the same techniques applied to boundary kinks and vertices.

14.1.4 Linactants

In two dimensions the growth of otherwise unfavoured crystal faces can be encouraged by the use of surfactants; surface active agents. These adsorbates, often required in only small quantities, work by lowering the surface energy of some or all facets. Perhaps analogous material could work with domain boundaries. These line active
agents, linactants, would decrease the line energy of domain boundaries. In fact, linactants have only recently been demonstrated on a macroscopic scale for stabilizing the boundaries between phases of 2D molecular monolayers [186].

How might such linactants work for domain boundaries? Crudely speaking, a surface restricted, but mobile, adsorbate has two possible places to reside; within a domain or at a domain boundary. In either location there will generally be an activation barrier to the global minimum configuration. Boundary segregation will occur in cases where the energy of the decorated boundary is lower than that for the decorated domain interior. In such cases the only things preventing the introduction of more domain boundaries are kinetic: there is an energy barrier, and topological restriction to the introduction of new boundaries. However, to some extent, both of these can be overcome by increasing the temperature. In the first case because higher temperatures increase the Boltzmann factor and the likelihood of surmounting the energy barrier, and in the latter case because, for the same reasons, higher temperatures increase the mobility of boundaries and allow them to shift into arrangements which present the most favourable boundaries.

This might be called the strong regime of linactant activity. In this case the energy of the decorated domain boundary is lower than that of the domain interior (i.e. $\lambda < 0$), so the system wants to introduce domain boundaries. This can be contrasted with the weak regime where decoration of boundaries of one character is preferred over another, but neither is energetically preferred to the domain interior. In this case the linactant encourages the growth of one boundary type over the other, but boundaries are still discouraged since $\lambda > 0$. It is questionable whether the second regime could ever exist; a linactant’s activity is dependant on it actually being present.
at the boundary, and if its energetically preferred location is at the domain interiors then the boundaries will remain bare, and inactivated.

The principles described above are the same introduced when discussing the non-uniform distribution of boundary characters in Ch. 11. The addition of an adsorbate adds two complications. The first is that it is important to ensure that the temperature remains below that necessary for a phase transition within the domain interior to a new, globally minimum, reconstruction. The second, more useful difference, is that the species of adsorbate and the details of its bonding at the boundary will dictate which of the boundaries is favoured. So, with care, linactants could be made to favour specific boundaries rather than all boundaries.

In fact, the growth of magic clusters on boundaries demonstrates these principles. The observed segregation of In/Ga to the B[22] boundaries shows that to be the lower energy configuration. Once all the B[22] boundaries are filled, the adsorbates cover other boundaries, and eventually the domain interior. However, if B[22] boundaries could be easily created, the lowest energy solution would be for more of them to appear to accommodate any extra adsorbate, rather than forcing it onto other boundaries. The reason this doesn’t happen in practice is that the growth temperature is too low to allow boundary movement and dissociation. So the surface is stuck with the boundaries it had before the adsorbate was introduced. This temperature is restricted by the formation of the $\sqrt{3} \times \sqrt{3}$ reconstruction which is the global energy minimum for these coverages.

Two changes in the preparation might allow true linactant mediated growth. The first is to choose an adsorbate with a higher transition temperature to the $\sqrt{3} \times \sqrt{3}$ phase. Aluminum fits this criterion. Its transition to $\sqrt{3}$, at least for Si(111), is at
the same temperature as the annealing step in SPE when the boundaries are mobile. The other modification is to introduce the linactant to the amorphous Ge overlayer before annealing in the SPE process. In this way, if the adsorbate floats to the surface, it can stabilize boundaries as they form.

Consider what would happen if linactant mediated growth were possible in the manner described. If it is strong enough the surface is now covered with B[22] boundaries alone. In the absence of symmetry breaking the network of boundaries will have a hexatic structure. Vicinal surfaces could be used to stabilize boundaries running in a specific direction. What if there was an cluster growing adsorbate that preferred the unfaulted rather than faulted HUC? Linactant mediate growth in the presence of that adsorbate would favour the formation of A[02] or A[20] boundaries since they maximize the density of UHUCs.

14.2 Summary

This work covered two main areas. First, it presented a detailed investigation of the boundaries that form between domains of the 5×5 reconstruction. Solid phase epitaxy was shown to be effective at generating a high density of domain boundaries that were straight and well-ordered. A nomenclature for identifying them was expanded to include the new B-type boundaries not seen before on 7×7, and a catalog was collected of all the observed boundaries along with proposed atomic structures. Registration with the substrate insists that the characters of domain boundaries near one another obey certain relationships. These relationships, and example STM images, were presented for boundary kinks and vertices. The distribution of domain boundary characters is not uniform, and there are a small number of boundary types
which dominate the others. This was proposed to reflect the relative energies of the different types of boundaries. Different kinetic processes were advanced that could be used to evolve from a uniform distribution to the peaked one observed.

This work’s second contribution was to reiterate the importance of substrate structure for the growth of surface magic clusters, and to exploit that importance by using domain boundaries to pattern 1D arrays of nanostructures. Magic clusters do not form on \(5 \times 5\) because the atomic structure of the HUC is incommensurate with their formation. However, on the boundaries with quasi-\(7 \times 7\) unit cells, In and Ga adsorbates cluster magically in a 1D pattern defined by the boundary. This suggests a new technique for atomic scale patterning of 1D features that could be extended to other reconstruction domain boundaries and cluster types.
Bibliography


Appendix A

The Cold Stage

A major upgrade undertaken in the course of this work was the introduction of a cryogenic system to allow cooling of the STM sample. The primary responsibility for this lay with M.Sc. student Jason Visser under the supervision of the author, but significant input was provided by Jay Weymouth and Ben Drevniok. The system design goals were:

- A base temperature with LN₂ cryogen of <100 K
- Low vibration operation compatible with STM imaging
- Retrofit to existing STM system with minimal disruption

The final design, shown in Fig. A.1, uses a commercial continuous flow cryostat (APD) connected to a modified sample stage via a copper braid. The braid comprises some 9000 annealed high purity copper wires each 0.001" in diameter (California Fine Wire). This provides a thermal link between the cryostat and stage, but maintains the necessary vibrational break between the stage and the chamber. Near its middle
APPENDIX A. THE COLD STAGE

Figure A.1: The Cold Stage. a) A photograph of the cold stage installed for testing. The cooling braid, teflon damper, and cyrostat are visible at the left. Extra thermocouple wires, used only for testing, are also visible. Photo courtesy of J. Visser. b) Schematic of the cold stage with sample holder in place. c) Reverse view with sample holder removed.
the braid is secured by a Teflon clamp to the bloc massif. This provides an intermediate vibration damping point, and is adapted from the scheme used by commercial Omicron microscopes. A heavy Cu dock, plated in Au, receives the sample holder. It sits upon a baseplate, also Au plated, to which the braid is bolted. A sapphire wafer between the dock and the baseplate, keeps the two electrically isolated so that a bias can be applied to the sample. The gold plating, the thinness and high thermal conductivity of the sapphire, and the huge cross-sectional area ensure excellent heat transfer across the sandwich. The assembly is stood off the bloc massif with PEEK screws and pins, which have exceedingly low thermal conductivity, arranged in an alternately pushing and pulling fashion to guard against loosening from thermal cycling [79].

Two tables are bolted to the top of the dock with a narrow gap between them. When the sample holder is slid onto the dock the sample, which is inclined like a ramp, fits into the gap and protrudes between the tables. The beetle, when lowered onto the tables, straddles the sample (two legs one side and one on the other) and walks in the up-ramp direction to approach. The tables are Mo, for good heat transfer and hardness, and polished for a smooth walking surface. One of the cold stage’s unique design features is a spring loaded plunger, shown in Fig. A.2, that pushes the sample holder upwards into tight contact with the tables. This provides excellent thermal contact between the two, eliminates rattling, simplifies transfers by securing the holder, and ensures consistent registration of the sample height relative to the tables and microscope. The plunger contacts the bottom of the sample holder through four PEEK rods, which are nonconductive, both thermally and electrically. To retract the plunger and release the sample holder, a manually actuated hook, which passes
Figure A.2: The Cold Stage Plunger. a) The plunger engaged. The plunger pins, driven by the spring, force the sample holder upwards against the tables. There is no contact between the hook and loop. b) The plunger disengaged. The hook engages the loop pulling the plunger down. The sample holder new rests lightly against the rail of the dock and is ready to be removed.

up through the vibration damping stack, engages a loop on the plunger and pulls it down against the spring. When the plunger is in use for scanning, the hook and the loop disengage and there is no mechanical connection between the sample stage and the chamber, except through the damping stack.

A.1 Cold Stage Measurements and Models

The cold stage was subjected to tests of its vibration stability, temperature equilibration between the various components, base temperature, and cooldown time. Tests with multiple thermocouple show that thermal equilibration between the different components is excellent. All of the components of the sandwich stay within 1 K of
one another. The sample itself is always <5 K higher than the cold stage temperature. Aside from good sample cooling, this means that the sample temperature can be inferred from the stage temperature with reasonable precision. A typical cooling cycle is shown in Fig. A.3 showing the temperature of the cryostat, and stage from measurements and simulation. The lowest temperature recorded here is 116 K which implies a sample temperature of ~120 K. The cooldown time, taken to be time to reach 98% of base temperature, is 3.8 hrs. Surprisingly, there is variation between the measured temperature profiles of different cryostat runs, even when the system configuration remains unchanged. For instance, the lowest base temperature observed is 109 K, somewhat lower than that for the run shown in Fig. A.3, even with similar wait times.

Images like that shown in Fig. A.4 confirm the vibrational stability of the system. It shows a Si(111)7×7 surface with islands of adsorbed Ge taken with the sample at ~114 K. The important point for the discussion here is that the resolution and noise
Figure A.4: Imaging at Low Temperature. Si(111) 7×7 with Ge islands at 114 K.

are both qualitatively comparable to those seen during room temperature operation, and without the added vibrational links introduced by the cold stage modifications. A simple numerical model was developed to explain the cold stage temperature profiles based on four parameters: the thermal conductivity of the braid $k_b$, the thermal conductivity of the standoff screws $k_c$, the coupling constant for radiation $k_r$, and the thermal mass of the stage $C$. Based on these the evolution of the cold stage temperature $T_{CS}(t)$ can be calculated based on the measured temperatures at the cryostat head $T_{cryo}(t)$, and room temperature $T_{RT}$ based on the following differential equation

$$C \frac{dT_{CS}}{dt} = k_c(T_{RT}(t) - T_{CS}(t)) + k_r(T_{RT}^4(t) - T_{CS}^4(t)) + k_b(T_{cryo}(t) - T_{CS}(t)). \quad (A.1)$$

The terms on the right are all heat gains and losses. The first is the heat gain, based on the heat equation, due to conduction through the mounting screws, the
second, based on the Stefan-Boltzmann law, is the heat gain due to radiation from the chamber, and the third is the heat extracted through the braid by the cryostat. The temperature of the stage will change based on the balance of these heats. The complete temperature profile of the cold stage $T_{CS}(t)$ can be simulated based on the measurements of $T_{cryo}(t)$ and $T_{RT}$. The parameter values which minimize the weighted $\chi^2$ of the simulation versus the measured cold stage temperature are the best fit parameters. These four parameters over-determine the system, so any one of them must be fixed before the other’s values are established. Each of the four parameters can be independently calculated. For instance, $k_b$ of the braid can be calculated from the thermal conductivity of copper, the length of the braid, the cross section of each wire and the number of wires. But of all of them, the thermal mass of the system $C$ is the one least subject to uncertainties and for which the most reliable inputs are available. Thus, we use $C$ as our fixed parameter, and scale the other three appropriately.

A simulation of the temperature cycle shown in Fig. A.3 by the dashed line. The model, although crude, provides reasonable agreement with the measured temperature profiles. Table A.1 shows a comparison of the values determined from the simulation and from geometrical calculations. The uncertainties reflect the unexplained differences in observed temperature profiles. There is order of magnitude agreement for $k_r$ and $k_b$, but $k_c$ is significantly higher than predicted. The simplest explanation for this is that the thermal conductivity is only calculated for the low conductivity PEEK fasteners that support the stage. The estimate does not include the various wires that also connect to the stage and increase the heat gain. The model indicates that radiation plays an unimportant role in the system base temperature, and that
Table A.1: Simulation Parameters. The values were calculated according using the design geometry and physical properties, and as best fits to the experimental temperature data. The heat capacity $C$ was fixed in the simulation to match the geometric value.

Improvements can be seen by identifying and reducing the conductive losses.
Appendix B

Vector Math in a Hexagonal Basis

The fcc(111) surface has hexagonal symmetry, and it is natural to work in a basis where the unit vectors are compatible with the surface. Unfortunately this is not an orthogonal basis, so some of the results from linear algebra that take orthogonality for granted will only work with some modification. This appendix explicitly describes some of the common tools of linear algebra in the hexagonal coordinate system.

B.1 The Unit Vectors

In terms of Cartesian coordinates the following unit-length vectors will form the basis of the hexagonal coordinate system:

\[ a_1 = \frac{\sqrt{3}}{2} \hat{x} - \frac{1}{2} \hat{y} \]  

(B.1)

and

\[ a_2 = \frac{\sqrt{3}}{2} \hat{x} + \frac{1}{2} \hat{y}. \]  

(B.2)
APPENDIX B. VECTOR MATH IN A HEXAGONAL BASIS

A vector like $\mathbf{v} = 2\mathbf{a}_1 + 3\mathbf{a}_2$ can be written in shorthand as $\mathbf{v} = [2 3]_h$. And, if the hexagonal basis is implicit, in even shorter hand as $\mathbf{v} = [2 3]$. For this appendix, which will skip back and forth between hexagonal and Cartesian coordinates, the subscript $h$ will be kept explicit, but in the main text it will be left off. Row vectors will be used inline. However for matrix multiplication, the row vectors will be replaced with column vectors.

One of the downsides to the hexagonal basis is that vectors which are equivalent to one another often appear from their indices to be different, and vectors which are different appear to be equivalent. For instance $[1 0]_h$, $[\bar{1} 1]_h$, and $[0 \bar{1}]_h$ are all crystallographically equivalent; being related by 120° rotations. So too are $[1 1]_h$ and $[\bar{2} 1]_h$. But, $[1 1]_h$ and $[\bar{1} 1]_h$ are not the same, even though they look like they are. This problem of camouflaged equivalence could be solved by using Miller-Bravais index notation, but rather than introducing a third index, the notation will be kept simpler at the risk of insisting on closer watchfulness.

### B.2 Changes of Basis

To convert from the hexagonal basis to the Cartesian one use the basis transformation matrix

$$
\mathbf{A} = \begin{pmatrix}
[a_1] [a_2]
\end{pmatrix} = \begin{pmatrix}
\frac{\sqrt{3}}{2} & \frac{\sqrt{3}}{2} \\
-\frac{1}{2} & \frac{1}{2}
\end{pmatrix}.
$$

(B.3)

To get from hexagonal $\mathbf{v}_h$ to Cartesian $\mathbf{v}_c$ just

$$
\mathbf{v}_c = \mathbf{A} \mathbf{v}_h.
$$

(B.4)
APPENDIX B. VECTOR MATH IN A HEXAGONAL BASIS

So

\[
\begin{pmatrix}
\frac{\sqrt{3}}{2} & \frac{\sqrt{3}}{2} \\
-\frac{1}{2} & \frac{1}{2}
\end{pmatrix}
\begin{pmatrix}
1 \\
1
\end{pmatrix}_h = \begin{pmatrix}
\sqrt{3} \\
0
\end{pmatrix}_c.
\]

(B.5)

To convert back use the inverse

\[
A^{-1} = \begin{bmatrix}
\frac{1}{\sqrt{3}} & -1 \\
\frac{1}{\sqrt{3}} & 1
\end{bmatrix}.
\]

(B.6)

B.3 The Dot Product

In Cartesian coordinates

\[
v_c \cdot u_c = v_c^T u_c = v_1 u_1 + v_2 u_2.
\]

(B.7)

To find an expression for the dot product in hexagonal coordinates, simply perform a change of basis on the two vector to convert them to Cartesian coordinates, and then use the above formula;

\[
v_h \cdot u_h = (Av_h)^T (Au_h)
\]
\[
= v_h^T A^T Au_h
\]
\[
= v_h^T \begin{bmatrix}
1 & \frac{1}{2} \\
\frac{1}{2} & 1
\end{bmatrix} u_h
\]
\[
= v_1 u_1 + \frac{1}{2}(v_1 u_2 + v_2 u_1) + v_2 u_2.
\]
B.4 Translation

Translating a vector \( \mathbf{v} \) by a vector \( \mathbf{u} \) is simply a case of adding the two together. So the translation operator \( \hat{T}_u \) is

\[
\hat{T}_u \mathbf{v} = \mathbf{v} + \mathbf{u}
\]  

(B.8)
in either basis.

B.5 Rotation

The rotation matrix in Cartesian coordinates is

\[
R_c(\theta) = \begin{bmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta
\end{bmatrix}.
\]

(B.9)

The hexagonal version is found from

\[
R_h(\theta) = A^{-1} R_c A
\]

\[
= \begin{bmatrix}
\cos \theta - \frac{1}{\sqrt{3}} \sin \theta & -\frac{2}{\sqrt{3}} \sin \theta \\
\frac{2}{\sqrt{3}} \sin \theta & \cos \theta + \frac{1}{\sqrt{3}} \sin \theta
\end{bmatrix}.
\]

So, for instance,

\[
R_h(60^\circ) = \begin{bmatrix}
0 & -1 \\
1 & 1
\end{bmatrix},
\]

(B.10)

and

\[
R_h(60^\circ) \mathbf{a_1} = \begin{bmatrix}
0 & -1 \\
1 & 1
\end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \mathbf{a_2}.
\]

(B.11)
B.6 Reflection

In Cartesian coordinates, the matrix for reflection in a line $l_c$ which passes through the origin is given by

$$M_c = \frac{1}{l_x^2 + l_y^2} \begin{bmatrix} l_x^2 - l_y^2 & 2l_x l_y \\ 2l_x l_y & l_y^2 - l_x^2 \end{bmatrix}.$$  \hfill (B.12)

To convert to hexagonal coordinates

$$M_h(l) = A^{-1} M_c A.$$  \hfill (B.13)

It is also necessary to use the change of basis formula from above to convert express the components of $l$ in terms of $a_1$ and $a_2$ rather than $x$ and $y$. This gives

$$M_h(l) = \frac{1}{l \cdot l} \begin{bmatrix} l_1^2 - l_2^2 & l_1(l_1 + 2l_2) \\ l_2(2l_1 + l_2) & -l_1^2 + l_2^2 \end{bmatrix}.$$  \hfill (B.14)

So a reflection in the y-axis, $l_h = [\bar{1} 1]$ is given by

$$M_h([\bar{1} 1]) = \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix},$$  \hfill (B.15)

and, as an example

$$M_h([\bar{1} 1]) a_1 = \begin{bmatrix} 0 & -1 & 1 \\ -1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 \\ -1 \end{bmatrix} = -a_2.$$  \hfill (B.16)
B.7 Shift Vectors

The shift vectors, which describe the mismatch between two DAS domains, require special treatment. By convention, their components are always written as the symmetric modulo with respect to $N$ the size of the unit cell. So they are an integer within the range $-(N-1)/2, -(N-1)/2 + 1, \ldots -1, 0, 1, (N-1)/2 - 1, (N-1)/2$.

The symmetric modulo can be found from the conventional modulo, $\text{mod}_N(a)$, as

$$\text{mods}_N(a) = \text{mod}_N(a - \frac{1}{2}(N+1)) + \frac{1}{2}(N-1).$$ (B.17)

So, for instance, the result of translating a shift vector $S = [2 1]$ on $5 \times 5$ through $v = [1, 6]$ is

$$T_vS = \begin{bmatrix} 1 \\ 6 \end{bmatrix} + \begin{bmatrix} 2 \\ 1 \end{bmatrix} = \text{mods}_5 \begin{bmatrix} 3 \\ 7 \end{bmatrix} = \begin{bmatrix} -2 \\ 2 \end{bmatrix}. $$

B.7.1 Multiplication and Division Modulo $N$

If $a \equiv b \text{ (mods}N)$ and $m \equiv n \text{ (mods}N)$ then $ma \equiv nb\text{(mods}N)$. Thus, $ma \equiv na\text{(mods}N)$. In general, the multiplier $m$ will be expressed on the range $-(N-1)/2 \ldots (N-1)/2$ just like the multiplicand $a$. 

APPENDIX B. VECTOR MATH IN A HEXAGONAL BASIS

For division, the situation is more complicated. If

\[ a \equiv \frac{b}{n}\mod(n), \quad (B.18) \]

where \( n \) is an integer, then it is also true that

\[ a \equiv \frac{b}{n}(1 + mN)\mod(n), \quad (B.19) \]

since \( 1 + mN \equiv 1\mod(n) \), if \( m \) is another integer. Thus it is simply necessary to find a numerator \( 1 + mN \) which is evenly divisible by \( n \). That is

\[ 1 + mN \equiv 0\mod(n). \quad (B.20) \]

Once the appropriate numerator is found \( (1 + mN)/n \) is an integer and the situation can be handled in the same manner as multiplication. Note that \( n \) being a multiple of \( N \) is equivalent to dividing by zero.

For an example, if

\[ a \equiv \frac{b}{7}\mod(5) \]

\[ \equiv \frac{1 + 5m}{7}b\mod(5). \]

For \( m = 4 \), \( (1 + 5m)/7 = 3 \), so

\[ a \equiv 3b\mod(5) \]

\[ \equiv -2b\mod(5). \]
In general, for the sake of compactness, relationships like those above will be written as equalities \((a = b)\) rather than as congruences \((a \equiv b (\text{mods} 5))\), when from the context it is clear that the arithmetic is subject to modulo, and the modulus is obvious.
Appendix C

Vertex Catalog

This appendix provides a complete list of the unique vertices for kinks (2-Vertices) and 3-Vertices.

C.1 Complex Number Formulation of Vertex Notation

In Ch. 10 a notation for vertices was introduced where, for each boundary, the characters A and B identify the type of the boundary, and left- and right-pointing under-arrows indicate its direction of propagation with respect to the vertex. So, for instance $\vec{A}$ indicates an A-type boundary whose direction of propagation points away from the vertex. This scheme has the advantage of transparency (it’s easy to identify what the notation means), but manipulation can be difficult, often resorting to look-up tables. Another formulation, using complex numbers, makes manipulation simple, but sacrifices some transparency.
In complex notation the two types of boundaries, A and B, are identified by 1 and $i$ respectively. The boundary direction is indicated by the sign, + for away from the vertex, - for towards. Thus, the four possibilities are

$\bar{A} = +1$, $\bar{A} = -1$, $\bar{B} = i$, $\bar{B} = -i$.

Rotations by 30° are achieved by multiplying by $-i$. So

$$\mathbf{R}(30^\circ) \bar{A} = (-i)(+1) = -i = \bar{B}, \quad (C.1)$$

and

$$\mathbf{R}(90^\circ) \bar{A} = (-i)^2(+1) = i = \bar{B}. \quad (C.2)$$

Reflections in A-type boundaries correspond to reflection in the real axis, found by taking the reciprocal. For example

$$\mathbf{M}_A \bar{A} = \frac{1}{-1} = 1, \quad (C.3)$$

and

$$\mathbf{M}_A \bar{B} = \frac{i}{-1} = -i. \quad (C.4)$$

Reflections in B-type boundaries are reflections in the imaginary axis, calculated by negating the reciprocal. For instance

$$\mathbf{M}_B \bar{A} = (-1)\frac{1}{-1} = -1, \quad (C.5)$$

and

$$\mathbf{M}_B \bar{B} = (-1)\frac{i}{-1} = i. \quad (C.6)$$
APPENDIX C. VERTEX CATALOG

| Rotation by $n \times 30^\circ$ | $R(n \times 30^\circ)X$ | $(−i)^nX$ |
| Reflection in A-type axis | $M_A X$ | $X^{-1}$ |
| Reflection in B-type axis | $M_B X$ | $−X^{-1}$ |

**Table C.1: Vertex Plane Isometries in Complex Notation.**

These operations are summarized in Table C.1.

Entire vertices can be written in this way by substituting complex numbers for the character symbols used previously. So

$$\vec{A}_{210} \vec{B}_{150} \vec{A} \rightarrow 1^{210} \cdot i^{150} 1$$ \hspace{1cm} (C.7)

and

$$\vec{B}_{210} \vec{A}_{90} \vec{B}_{60} \vec{B} \rightarrow i^{210} − 1^{90} − i^{60} i$$ \hspace{1cm} (C.8)

### C.2 Kink Catalog

Kinks with the same angles between the boundaries comprise a class containing four members. The classes are labeled according to the angle of deviation, i.e. $180^\circ$ minus the smallest vertex angle. The only symmetric kink is $X_{180}X_{180}X$ which is a straight boundary. There are 20 unique kinks.

The kink classes are presented in the tables below, along with the corresponding relationships between the indices of the two segments. Kinks which differ only in the direction of their members have the same index relations, but are different structures.
C.3 3-Vertex Catalog

There are twelve different classes of 3-boundary vertices. Five of those classes are mirror-symmetric vertices (those have two or more equal angles). These contain four distinct vertices. The remaining seven, non-symmetric classes contain eight members. There are 20 unique symmetric vertices, and 52 asymmetric ones, although many of these are statically unstable.

The vertex classes are labelled as $X_\alpha Y_\beta Z_\gamma X$ with a convention that $\alpha \geq \beta$, and $\beta \geq \gamma$. All other vertices can be found by permuting the order of angles through reflection. Written this way the ranges for the angles are restricted to be $120^\circ \leq \alpha \leq 360^\circ$.

<table>
<thead>
<tr>
<th>30°</th>
<th>60°</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{210} \rightarrow B_{150} \rightarrow A$</td>
<td>$A_{240} \rightarrow A_{120} \rightarrow A$</td>
</tr>
<tr>
<td>$A_{210} \rightarrow B_{150} \rightarrow A$</td>
<td>$A_{240} \rightarrow A_{120} \rightarrow A$</td>
</tr>
<tr>
<td>$B_{210} \rightarrow A_{150} \rightarrow B$</td>
<td>$B_{240} \rightarrow B_{120} \rightarrow B$</td>
</tr>
<tr>
<td>$B_{210} \rightarrow A_{150} \rightarrow B$</td>
<td>$B_{240} \rightarrow B_{120} \rightarrow B$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>90°</th>
<th>120°</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{270} \rightarrow B_{90} \rightarrow A$</td>
<td>$A_{300} \rightarrow A_{60} \rightarrow A$</td>
</tr>
<tr>
<td>$A_{270} \rightarrow B_{90} \rightarrow A$</td>
<td>$A_{300} \rightarrow A_{60} \rightarrow A$</td>
</tr>
<tr>
<td>$B_{270} \rightarrow A_{90} \rightarrow B$</td>
<td>$B_{300} \rightarrow B_{60} \rightarrow B$</td>
</tr>
<tr>
<td>$B_{270} \rightarrow A_{90} \rightarrow B$</td>
<td>$B_{300} \rightarrow B_{60} \rightarrow B$</td>
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<table>
<thead>
<tr>
<th>150°</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{330} \rightarrow B_{30} \rightarrow A$</td>
<td>$X_\alpha Y_\beta Z_\gamma X$</td>
<td>$A_{330} \rightarrow B_{30} \rightarrow A$</td>
</tr>
<tr>
<td>$A_{330} \rightarrow B_{30} \rightarrow A$</td>
<td>$A_{330} \rightarrow B_{30} \rightarrow A$</td>
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<td>$B_{330} \rightarrow A_{30} \rightarrow B$</td>
<td>$B_{330} \rightarrow A_{30} \rightarrow B$</td>
</tr>
</tbody>
</table>

C.3 3-Vertex Catalog
300; \( \beta \geq 180^\circ - \frac{1}{2}\alpha \) and \( \beta \leq \alpha \) and \( \beta \leq 330^\circ - \alpha \); and \( \gamma = 360^\circ - \alpha - \beta \). Statically stable vertices are those for which \( \alpha \leq 180^\circ \). These are marked with asterisks.

<table>
<thead>
<tr>
<th>*X_{120}X_{120}X_{120}X</th>
<th>*X_{150}Y_{150}X_{60}X</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \overrightarrow{A}<em>{120} \overrightarrow{A}</em>{120} \overrightarrow{A}_{120} \overrightarrow{A} )</td>
<td>( \overrightarrow{A}<em>{150} \overrightarrow{B}</em>{150} \overrightarrow{A}_{60} \overrightarrow{A} )</td>
</tr>
<tr>
<td>( n - p - q + s = 0 )</td>
<td>( m + p + q - r = 0 )</td>
</tr>
<tr>
<td>( \overrightarrow{A}<em>{120} \overrightarrow{A}</em>{120} \overrightarrow{A}_{120} \overrightarrow{A} )</td>
<td>( \overrightarrow{A}<em>{150} \overrightarrow{B}</em>{150} \overrightarrow{A}_{60} \overrightarrow{A} )</td>
</tr>
<tr>
<td>( m + p - r - s = 0 )</td>
<td>( \overrightarrow{B}<em>{150} \overrightarrow{A}</em>{150} \overrightarrow{B}_{60} \overrightarrow{B} )</td>
</tr>
<tr>
<td>( \overrightarrow{A}<em>{120} \overrightarrow{B}</em>{120} \overrightarrow{A}_{120} \overrightarrow{B} )</td>
<td>( \overrightarrow{A}<em>{150} \overrightarrow{B}</em>{150} \overrightarrow{A}_{60} \overrightarrow{A} )</td>
</tr>
<tr>
<td>( \overrightarrow{B}<em>{120} \overrightarrow{B}</em>{120} \overrightarrow{B}_{120} \overrightarrow{B} )</td>
<td>( \overrightarrow{B}<em>{150} \overrightarrow{A}</em>{150} \overrightarrow{B}_{60} \overrightarrow{B} )</td>
</tr>
<tr>
<td>( n - q + r + s = 0 )</td>
<td>( n + q + r + s = 0 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>*X_{180}X_{90}Y_{90}X</th>
<th>X_{240}X_{60}X_{60}X</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \overrightarrow{A}<em>{180} \overrightarrow{A}</em>{90} \overrightarrow{B}_{90} \overrightarrow{A} )</td>
<td>( \overrightarrow{A}<em>{240} \overrightarrow{A}</em>{60} \overrightarrow{A}_{60} \overrightarrow{A} )</td>
</tr>
<tr>
<td>( n - p - r = 0 )</td>
<td>( n + q + r + s = 0 )</td>
</tr>
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### APPENDIX C. VERTEX CATALOG

#### *X*$_{150}$ *Y*$_{120}$ *Y*$_{90}$ *X*

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#### *X*$_{180}$ *X*$_{150}$ *Y*$_{30}$ *X*$_{210}$ *Y*$_{120}$ *Y*$_{30}$ *X*$_{210}$

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### APPENDIX C. VERTEX CATALOG

### X\textsubscript{210}Y\textsubscript{90}X\textsubscript{60}X

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### X\textsubscript{270}Y\textsubscript{30}X\textsubscript{60}X

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