ENERGETICALLY AND KINETICALLY DRIVEN STEP FORMATION AND EVOLUTION ON SILICON SURFACES

DISSERTATION

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ABSTRACT

Energetically and kinetically driven step formation and evolution on Si(001) and Si(111) surfaces has been investigated experimentally using scanning tunneling microscopy (STM), atomic force microscopy (AFM), optical microscopy, and low-energy electron microscopy (LEEM). Four systems are investigated:

(1) Detailed STM measurements of boron-doped Si(001) surfaces is presented, along with large-scale AFM and LEEM observations of the well-known boron-induced ‘striped’ phase at elevated temperatures. Boron is shown to induce a variety of related atomic-scale structures, some of which tend to decorate surface step-edges. This, in turn, could provide an explanation for the observed boron-induced reduction in step formation energy. However, the observed boron-accumulation at step-edges does not appear to vary systematically with annealing temperature, leaving the well-known temperature dependence of the striped phase unresolved. Real-time LEEM observations of striped step formation on Si(001) during diborane (B₂H₆) exposure at elevated temperatures are used to demonstrate the controlled formation of large (>5µm) surface regions with highly uniform striped step structures.

(2) Large-scale step rearrangements have been investigated on Si(001) and Si(111) surfaces heated to sublimation temperatures (>900°C) using a direct current. These
surfaces undergo dramatic morphological changes, which are believed to arise from a directional drift of diffusing surface atoms in the presence of an applied electric field. Such ‘electromigration’ phenomena include step ‘bunching’ and step ‘wandering’, as well as a predicted step ‘bending’ instability. Using AFM and optical microscopy, we argue that the direction of surface atom electromigration on Si(001) can be parallel, antiparallel, or even sideways to the applied electric field, depending on the direction of the applied field with the high-symmetry <110> crystal directions. In addition, the first experimental evidence for the predicted step bending instability is presented.

(3) Sublimation pit formation is studied on Si(001) surfaces heated to ~1000°C. Real-time LEEM and microscopic modeling of step dynamics is used to show that – for a given net sublimation rate – adding a small Si flux during heating increases the stability of atomically flat surface terraces against sublimation pit formation. This makes it practical to produce much larger step-free terraces than have been reported previously.

(4) The anisotropy of surface diffusion on Si(001) has been analyzed from the formation of ‘denuded’ zones during Si(001) two-dimensional homo-epitaxial growth. Comparison with a simple model for surface atom diffusion shows that diffusion is at least 10 times faster along the surface ‘dimer’ rows than across them. Furthermore, contrary to previous reports, Si(001) surface diffusion is shown to be anisotropic at temperatures up to at least 850°C. The apparent contradiction between our results and
those reported by previous authors is resolved by observing denuded zone formation for several different growth conditions.
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CHAPTER 1

INTRODUCTION

1.1 Introduction

Characterizing and controlling the morphology of semiconductor surfaces is one of the central topics of surface physics. The interest in this field stems not only from the desire to understand the fundamental atomic processes governing the evolution of crystal surfaces in general, but also from the need to control the surface and interface morphology of semiconductor device structures during growth and processing.

Ultimately, the shape and arrangement of atomic-height surface steps is the result of a competition between equilibrium thermodynamics and kinetically driven processes. On surfaces where the steps are in equilibrium with the two-dimensional “gas” of adsorbed diffusing surface atoms (“adatoms”) existing on the atomically flat terraces separating the steps, the arrangement of steps is determined by the thermodynamic properties of the steps themselves. However, under non-equilibrium conditions – such as during growth or evaporation – step evolution can be greatly influenced by the kinetics of adatom terrace transport and step-terrace-vapor adatom exchange. The task of understanding and
predicting the evolution of crystal surfaces then becomes one of identifying the relative importance of energetically versus kinetically driven step formation and evolution.

In this Dissertation, I will offer several examples of step formation and evolution on the technologically important Si(001) – and to a limited extent Si(111) – surfaces. The surface studies presented here are primarily experimental in nature, and much of the data is in the form of atomic- and large-scale scanning tunneling microscopy (STM), atomic force microscopy (AFM), low-energy electron microscopy (LEEM), optical microscopy images of the surface, and microscopic modeling.

In Chapter 2, I will discuss energetically driven step formation on boron-doped Si(001) surfaces. Adding boron to Si(001) surfaces at elevated temperatures (>500°C) is known to induce spontaneous formation of extra surface steps via lowering of the surface step-edge creation energy, which in turn allows the surface to lower its average stress energy via stress relaxation at step edges. The steps thus formed arrange themselves into highly periodic, striped patterns, with a step spacing that is sensitive to both temperature and surface boron concentration. My study of this system is designed to address (i) the nature of the boron-induced step-edge energy-lowering mechanism, and (ii) whether it is practical, or even possible, to use the boron-doped Si(001) surface to manufacture highly periodic step structures of controllable spacing extending over macroscopic (tens of µm) distances. Such “gratings” could be of potential use in future semiconductor devices. To address these issues, I will present detailed atomic-scale STM measurements of the kind, density, and location of the various boron-related surface structures that form, and relate these observations to the observed large-scale (tens of nm) step structures. Our data shows that boron tends to decorate surface step-edges, which in turn could give clues to
precisely how boron lowers the step-edge energy. Using LEEM, I will also demonstrate that it is indeed possible – with care – to control the large-scale morphology of the boron-induced striped phase.

I will then discuss in Chapter 3 *kinetically* driven step rearrangement and large-scale (tens of nm to several μm) pattern formation on Si(001) and Si(111) surfaces heated to sublimation temperatures using resistive *direct current* (DC) heating. In this study, the step geometry on the surface and substrate temperature is such that little or no step formation occurs (via formation of sublimation pits). Rather, we are observing the rearrangement of existing steps into a variety of fascinating and visually striking step patterns. These patterns include (i) bunching of steps into “macro-steps” separated by large (several mm) nearly step-free terraces, (ii) wavy steps, with adjacent steps in-phase (step “wandering” patterns), and (iii) out-of-phase wavy steps (step “bending” patterns). These patterns, which can grow to macroscopic sizes and can often be observed with an optical microscope, are believed to arise from a directional drift of diffusing adatoms in the presence of the applied DC field. By observing the dependence of the occurrence of the various step patterns on the direction of the applied field with respect to (i) the <110> surface crystal directions, and (ii) the orientation of the step-edges and comparing these observations with existing theories for DC-induced pattern formation, we argue that the interaction between the applied field and the Si(001) diffusing surface atoms is surprisingly complex. In particular, we present evidence that the force exerted on an adatom by the applied field is highly anisotropic, such that the force can be parallel, anti-parallel, and even sideways to the direction of the applied field.
In Chapter 4, I will demonstrate how a fundamental understanding of step formation and evolution can be used to control surface morphology. In particular, I will discuss the controlled formation of monolayer (ML) - deep pits that form on Si(001) surfaces heated to sublimation temperatures (>950°C). Such pits form if the rate of desorption of adsorbed surface atoms (“adatoms”) on a terrace cannot be adequately compensated for by adatom formation from nearby step-edges. Hence, the stability of a terrace against pit formation depends sensitively on the rates of the various atomic processes occurring on the surface, such as the rate of adatom diffusion and the rate of adatom detachment for step-edges. We show, using LEEM and microscopic modeling, that adding a flux of Si atoms to the surface during sublimation enhances terrace stability for a given net sublimation rate. This opens up the possibility of producing ultra-large (~100 µm or larger) step-free Si(001) terraces, which could be of potential use in future devices for which the presence of surface steps has an adverse effect on performance.

Adatom diffusion rates strongly affect the observed behavior in the studies described above. For example, terrace stability against sublimation pit formation is highly sensitive to the rate at which adatoms can be transported from the step-edges bounding a terrace to the center of the terrace. Furthermore, the formation of a highly periodic, large-scale striped phase on boron-doped Si(001) surfaces turns out to be limited by transport of adatoms between regions of unequal adatom concentration. In Chapter 5, I will present measurements of the adatom diffusion anisotropy on Si(001) at intermediate temperatures (500-860°C). I will perform these measurements in the “conventional” way, i.e., by observing the anisotropies that arise in the distribution of ML-high (two-dimensional) Si islands that form during Si(001) homoepitaxial growth (i.e., epitaxy of Si on Si(001)).
Contrary to previously reported measurements, I show that adatom diffusion is anisotropic in this intermediate temperature range. Furthermore, I develop a simple model which gives quantitative agreement with the observed data, and which sets a lower limit on the diffusion anisotropy.

1.2 The Si(001)-(2×1) surface

Most of the work in this Dissertation centers on the Si(001)-(2×1) reconstructed surface. The unreconstructed Si(001)-(1×1) surface consists of atoms arranged on a square lattice with spacing \( a/\sqrt{2} \) (where \( a = 5.43 \) Å is the Si fcc unit cell, as shown in Fig. 1.1 (a)), with the atomic rows oriented along the \(<1\bar{1}0>\) crystal directions. Each atom has two “back” bonds lying in the (110) plane and directed toward the bulk atoms, as well as two “dangling” surface bonds lying in the (1\bar{1}0) plane. The (2×1) “dimer” reconstruction arises when neighboring surface atoms bond together, thereby reducing the density of energetically costly dangling bonds. As a result, the position of an atom deviates somewhat from its position on an unreconstructed Si(001) surface. The resulting dimer rows are oriented along the \(<1\bar{1}0>\) crystal directions, as shown in Fig. 1.1 (b). The (2×1) dimer reconstruction is the surface reconstruction that is normally observed on Si(001) surfaces that have been cleaned in ultra-high vacuum (UHV) (\(\sim 10^{-10} \) Torr) by heating the surface to temperatures near 1200°C, which is the conventional way of preparing Si(001) surfaces for atomic-scale studies. Note that other surfaces, such as the (110) and (111) surfaces, can be prepared in-situ by cleaving the wafer (at room temperature) in UHV.
Since the orientation of the tetrahedrally oriented Si bonds alternates between the [110] and [1\bar{1}0] crystal directions, the dimer row direction rotates 90° when crossing a ML-high surface step. This gives rise to two kinds of ML-high (“single height”) steps on the Si(001) surface, where a ML corresponds to a surface height change of \(a/4\). “A-type” (“B-type”) single-height steps (designated \(S_A\) (\(S_B\))) are steps where the dimer rows on the upper terrace are oriented parallel (perpendicular) to the step-edge. Note that single-height surface steps are the type of steps normally present on vicinal Si(001) surfaces, as long as the surface misorientation (“miscut”) away from [001] is less than about 2-4°. For higher miscuts, double-height steps are observed [1-4]. Fig. 1.2 and Fig. 1.3 show STM images of the Si(001)-(2×1) reconstructed surface. Note that these surface have in fact been doped with boron, and that undoped Si(001) surfaces do not usually exhibit such a high density of surface defects.

As a result of the (2×1) reconstruction, the Si(001) surface is known to be highly anisotropic in at least two distinct ways. First, the \(S_B\) step-edge chemical potential \(E_B\) (Gibbs free energy per step-edge site) is believed to be larger than the \(S_A\) step chemical potential \(E_A\). The ratio \(E_B/E_A\) can be measured directly from the shape of ML-high (two-dimensional) Si(001) islands [79], which are observed to be elliptical, with an increase in \(S_A\) step length favored over energetically costly \(S_B\) dimer row terminations. The fact that \(E_B/E_A > 1\) also means that the energy cost of creating “kinks” along \(S_A\) steps (i.e., short segments of \(S_B\) steps) is higher than that required for kink formation along \(S_B\) step-edges. As a result, surface steps that are “nominally” pure \(S_A\) steps are quite straight, whereas nominal \(S_B\) steps are relatively jagged (Fig. 1.4).
The second important anisotropy on Si(001)-(2×1) is that of diffusion of adsorbed Si atoms. We would expect the corrugation of the potential seen by a diffusing atom/dimer to reflect in some way the surface topography, and hence the location of the surface atoms. Indeed, diffusion of Si addimers on Si(001)-(2×1) has in fact been observed to occur almost exclusively along dimer rows at temperatures near room temperature. More will be said about Si addimer diffusion anisotropy in Chapter 5.

Thirdly, the (2×1) reconstruction puts the surface under stress, which furthermore is believed to be anisotropic. In particular, the surface stress is larger along the dimer bond than perpendicular to it. As a result, the surface stress tensor rotates 90° when crossing a single-height step.

Finally, we note that unlike Si(001), the Si(111) surface remains unreconstructed at the temperatures considered here (>900°C). As a consequence, Si(111) does not exhibit any anisotropies at these temperatures, and we expect both surface diffusion and step-edge properties to be isotropic with respect to the surface crystal directions.

1.3 Experimental techniques

1.3.1 Scanning tunneling microscopy

STM allows conducting surfaces to be imaged with atomic resolution. The components of an STM are illustrated schematically in Fig. 1.5. A sharp conducting tip is brought close to a conducting surface by means of one or several ultra-precise piezoelectric actuators, which give sub-Å control over tip-surface separation. Typical tip-surface separations during operation are in the Å-range. Application of a voltage (1-2 V)
between the surface (or “sample”) and the tip results in an electronic tunneling current, typically on the order of 1 nA. The STM images presented here are all taken in “constant current” mode. In this mode, the tip is raster scanned across the crystal surface while maintaining constant tunneling current (via a feedback loop). The signal that is actually recorded is not the tunneling current, but rather the voltage applied to the piezo-electric actuator required to maintain a constant tunneling current.

Note that STM gathers information about the surface only from the magnitude of the tunneling current, which is sensitive not only to surface topography, but also to the local density of electron/hole (or “filled” and “empty”) surface states. Hence, an STM image is a convolution of both topographical and electronic information. In the next chapter, we will see that the spatial distribution of filled and empty surface states can have a dramatic effect on the appearance of an STM image.

Also note that the key to the success of the STM is the strong exponential dependence of the tunneling current on tip-sample separation, which allows changes in tip-sample separation to be measured with sub-Å accuracy. Interestingly, the strong variation of tunneling current with tip-surface separation is also responsible for the unsurpassed lateral resolution of the STM. Ideally, one would like the tunneling current to originate from a single atom at the end of the metallic STM tip. However, since one usually has little control over the precise shape of these tips, a “typical” tip looks more like that shown in Fig. 1.5. Here, electrons tunnel to/from a large collection of atoms. Hence, the surface information gathered is effectively averaged over a large area, and the lateral resolution of the STM suffers. However, the unwanted lateral “smearing” caused by a blunt tip is compensated for by the strong exponential dependence of the magnitude
of the tunneling current on tip-sample separation. Hence, surface information is gathered at a well-defined point, and atomic lateral resolution becomes possible.

STM is well suited for surface studies on length scales from sub-nm to a few $\mu$m, and is used in the work discussed here primarily for investigating the atomic-scale properties of boron-doped Si(001) surfaces with the surface held at room temperature in UHV during scanning. All STM measurements presented here were made at Ohio State University. The STM used in these experiments has been described in detail elsewhere [5].

1.3.2 Atomic force microscopy

Like STM, AFM is a scanning probe microscopy technique where a probe is raster scanned across the surface and a topography is measured. In AFM, however, the probe is a sharp tip (usually Si or SiN) mounted on a flexible cantilever. As the tip is held at a fixed height (relative to the laboratory reference frame) and dragged across the surface, changes in cantilever deflection are detected using a laser beam that is bounced off the back of the cantilever. Hence, unlike STM, the surface to be studied does not need to be conducting. The AFM images presented here were obtained using a Digital Instruments Dimension3000 scanning probe microscope at the Ohio State University. The lateral resolution routinely achieved in the studies presented here is about 10 nm (using “tapping” mode), and the vertical resolution is sufficient to resolve single-height steps on Si(001) and Si(111) surfaces. Practical scan sizes are in the 1 – 100 $\mu$m range, which makes it ideal for investigating the large scale step structure on these surfaces. Note that all AFM images were obtained in air at room temperature, i.e., after removing the wafers
from the UHV chamber following thermal processing. Although a thin native oxide is known to form on silicon surfaces when exposed to air, this oxide is conformal and allows the underlying step structure to be imaged, provided the steps are at least 5-10 nm apart. AFM was used in this study primarily to investigate electromigration-induced step rearrangements following direct-current heating in UHV.

### 1.3.3 Real-time low-energy electron microscopy

LEEM [17] makes use of the low-energy electron diffraction (LEED) pattern formed when electrons backscatter elastically from a crystal surface. The energy of the incident electrons is only a few eV, and the information gathered from the surface is therefore highly surface sensitive. By placing an aperture at the point in the electron optics train where the 2-D diffraction pattern forms (i.e., in the back focal plane of the objective lens), a single diffraction spot can be selected for viewing. The image formed shows a contrast between the parts of the surface giving rise to the particular diffraction spot chosen, and the remaining surface regions. For example, when imaging the Si(001)-(2×1) surface, where neighboring terraces alternated between the (1×2) and (2×1) reconstruction (i.e., the dimer row direction rotates 90° when crossing a single-height step), the (1×2) and (2×1) surface regions produce physically distinct diffraction spots. By selecting the diffraction spot produced by the (1×2) terraces, these terraces will appear bright in the LEEM image, whereas the remaining (2×1) terraces appear dark. All LEEM images presented here are of the Si(001)-(2×1) surface.
The lateral resolution of LEEM is approximately 15 nm, and practical scan sizes range from a few μm up to at least 100 μm. Hence, LEEM is well suited for imaging surface steps, but does not give information about atomic-scale surface features. Furthermore, LEEM can be used to image the surface at any sample temperature, as long as the surface crystal structure remains intact. Hence, it is possible to observe in real-time how steps form and evolve. For the work presented here, LEEM was used to observe the stability of Si(001) terraces against pit formation during high-temperature sublimation, and for observing striped phase formation during exposure of flat Si(001) terraces to diborane at intermediate temperatures. The LEEM measurements were performed in conjunction with Hiroki Hibino and Changwu Hu at Arizona State University in the research lab of Prof. Ig Tsong.

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Fig 1.1. (a) The Si fcc unit cell. (b) Schematic illustration of the Si(001)-(2×1) surface.
Fig 1.2. STM image of the Si(001)-(2×1) reconstructed surface.
Fig 1.3. STM image of the Si(001)-(2×1) surface.
Fig 1.4. Large-scale STM image of a Si(001) surface. The “nominal” $S_B$ step is quite jagged, whereas the $S_A$ step is almost perfectly straight.
Fig 1.5. Schematic illustration of a scanning tunneling microscope.
CHAPTER 2

ENERGETICALLY DRIVEN STEP CREATION ON BORON-DOPED Si(001)

2.1 Introduction

A few years ago, Jones et al. [6] made the startling observation that ‘striped’ or ‘fingered’ step structures appear spontaneously on annealed, heavily boron-doped Si(001)-(2×1) surfaces. This striped phase is self-organized and highly periodic, with a spacing that can be ‘tuned’ by varying the sample temperature and/or changing the surface boron concentration [7,8]. This boron-induced step creation and ordering can be generally understood in terms of step-edge stress relaxation effects [9] which are enhanced by the boron-induced, temperature-dependent lowering of the local $S_A$-type step energy $E_A$ [7,10]. However, much remains to be understood about the atomic- and large-scale structure of the boron-doped Si(001) surface: (1) The precise atomic structure of boron on Si(001) has been under debate [11-14], (2) the mechanism by which boron decreases $E_A$ is not understood, and (3) boron-induced step formation on initially step-free surfaces has not been explored.
In this chapter, I will present three lines of investigation to address these important open issues: (1) Detailed bias-dependent STM measurements are used to characterize the boron-induced surface structures. This should aid the search for an atomic model, which in turn is necessary to investigate in what way, if any, boron changes the $S_A$-step creation energy and/or other surface properties. The observations presented in this Dissertation show that, contrary to previous reports [11], the boron-induced atomic-scale structures that form on *bulk* boron-doped surfaces are identical to those that form on surfaces that have been doped by heating in the presence of a diborane ($B_2H_6$) ambient pressure. (2) Using atomic-resolution STM measurements, the dependence of the surface boron concentration and the step-edge boron concentration on annealing temperature has been measured. A preferential accumulation of boron-related structures close to step edges is in fact observed, supporting the proposal that step-edge boron decoration could lower step energies. Surprisingly however, the overall surface boron concentration does *not* increase at lower annealing temperatures, leaving the striking temperature dependence of the spontaneous step formation observed on this system an open question. (3) LEEM is used to observe spontaneous step formation on initially *step-free* surfaces. I will argue that that surface evolution in this case is *kinetically* limited, limited by the free supply of diffusing Si addimers.

### 2.2 Experiment

The samples used in our STM measurements were either *bulk* boron doped Si(001) wafers or initially undoped wafers that were exposed to diborane at elevated temperatures. Both the bulk-doped (nominal resistivity of 0.001 $\Omega$-cm) and the initially
undoped wafers were provided by Virginia Semiconductor Company, and had a miscut less than .1° away from the [001] crystal direction. Prior to entry into the UHV chamber, the samples were either (i) rinsed with methanol, (ii) cleaned in an ultrasonic cleaner using trichloroethylene (TCE), acetone, and methanol (in that order), or (iii) cleaned in a UV-ozone cleaner. All cleaning methods produced similar results. For the STM measurements, samples were introduced into a UHV chamber (at the Ohio State University) equipped with an STM, an ion gauge, a residual gas analyzer, and an ion pump. Once inside the UHV chamber, the samples (and thus the sample-holder) were first degassed by heating to approximately 750°C for 6-12 hours. Performing the degassing at temperatures below 750°C ensures that the native oxide remains on the surface. This native oxide protects the Si(001) surface from contamination during sample/sample-holder degassing. The samples were heated resistively by passing a DC or AC current through them. Contact to sample was made through two molybdenum clips attached to the ends of the wafer. Typical sample dimensions are 15×2 mm, with a wafer thickness of ~1/4 mm. Sample temperature was measured with an infrared pyrometer, with an absolute uncertainty of +/- 9°C [5]. Prior to STM inspection, each sample was “flashed” several times at temperatures up to 1250°C. This aggressive heat treatment removes the native oxide and exposes an atomically clean Si(001) surface. All hot filaments (i.e., ion gauge and RGA filaments) were turned off during flashing to prevent contaminants released from such hot filaments to react with the wafer surface. Note that care must be taken to avoid sample melting during the flashing procedure. Since resistive heating is used, large temperature gradients can develop across the sample. These gradients are highly sensitive to the resistance of the wafer-moly clip contact, which can
change unpredictably. This is less of a problem for narrow samples, since the ratio of the contact resistance to the wafer resistance is smaller for narrow samples.

The initially undoped samples were doped with boron in a controlled manner by heating the wafers to temperatures in the 400-800°C range in a diborane \(10^{-9}-10^{-5}\) Torr atmosphere. The diborane partial pressure was precisely controlled by introducing the diborane into the UHV chamber through a variable leak valve. The pressure during diborane exposure was recorded from the ion pump current.

The STM experiments were done by annealing the boron-doped Si(001) wafers to temperatures in the 500-800°C range, and then quenching to room temperature. All STM measurements were done at room temperature.

For our LEEM observations, large, step-free Si(001) terraces were prepared by annealing Si(001) wafers patterned with arrays of square craters, which were provided by NTT, Japan, as well as by J. Blakely and C. Umbach at Cornell University. Heating at sublimation temperatures in ultra-high vacuum (UHV) causes closed steps on the crater floor to move toward the crater walls, leaving behind a large step-free terrace [15,16]. This flattening process will be discussed in detail in Chapter 4. Boron was added to these flat terraces by heating the wafers while exposing them to diborane at pressures in the range of \(10^{-9}\) to \(10^{-6}\) Torr. Using LEEM, we can observe the subsequent step formation in real-time, and record the results on video tape. LEEM produces a dark-bright contrast between adjacent Si(001) terraces separated by ML-high surface steps by selecting one of the \((\frac{1}{2},0)\) diffracted beams (due to the Si(001)-(2×1) dimer reconstruction) for imaging [17].
Note that for both the STM and LEEM experiments, a 1250°C flash generally returned the sample surface to nearly the same starting condition (step density, defect type and density, etc.), and a particular sample could therefore be cycled many times. Note that when an initially undoped Si(001) surface was exposed to diborane, a small residual amount of boron remained on the surface even after flashing.

2.3 Results

2.3.1 Atomic scale B/Si(001) structures

2.3.1.1 Bulk boron-doped Si(001) surfaces

To address the role of boron in the spontaneous formation of S_A-steps, detailed knowledge of how boron is incorporated at the Si(001) surface is required. Fig. 2.1 shows room-temperature STM images of the various B/Si(001) surface structures found after annealing bulk boron-doped Si(001) samples. Figs. 2.1(a) and (b) are filled and empty-state images, respectively, of the same sample area. The structure labeled ‘II’ is identical to that reported by Kulakov et al. [12] for bulk-doped Si(001). The type-II feature appears as a single oval-shaped protrusion between two dark “wings” in the filled-state image and as two roughly circular protrusions in the empty-state image. It covers an area of two dimer lengths in the direction parallel to the dimer rows times three dimer widths in the direction across dimer rows, i.e. it covers a 2×6 area. In addition, we believe the structure labeled ‘I’ is a related structure (it is only observed on boron-doped samples), and has an appearance that is similar to “one-half” of a type-II structure.
Figs. 2.1(c)-(f) show chains of three and four protrusions in empty-state images (labeled III and IV), as reported by Kulakov et al. Note that the type-I, II, III, and IV structures all display characteristic dark ‘wings’ in filled-state images. We believe the type-I feature should be viewed as the most basic building block for the various B/Si(001) structures observed. Note that the central protrusions in the type-III and IV features are brighter in empty-state images than the protrusions at the edges.

In addition, we believe the structure labeled G (for ‘Ghost’) in Figs. 2.1(a) and (b) is probably due to B. This structure takes on the appearance of two missing dimers in the filled-state image while appearing similar to normal Si dimers in the empty-state image. The type-G structure may be similar to a B-related feature reported by Komeda et al. [18], which they reported to appear dark (normal) in filled- (empty-) state images, respectively. However, we believe that the structure reported by Komeda was incorrectly identified, and was most likely just the “wing” of a type-I, II, III, or IV structure, which also appears dark (normal) in filled- (empty-) state images. In our case, it is clear that the type-G structure seen in Figs. 2.1(a) and (b) is not simply the “wing” of a nearby type-I, II, III, or IV structure.

Of the various boron-induced structures considered, the type-II structure is the most common, outnumbering the type-I by about 2:1, the type-G by 4:1, and the type-III by 20:1. The type-IV is only occasionally observed. Quantitative counting results will be discussed later.

Fig. 2.1 also shows several distinct variations on the type-II structure, which we believe are essential to the complete understanding of B/Si(001) surface chemistry. These are (i) the feature marked ‘II-1w’ (‘1 wing’) in Figs. 2.1(c) and (d), which has only
one dark wing in the filled-state image, (ii) the feature ‘II-bd’ (‘bright-dim’) that has one protrusion brighter than the other in filled-state images, and (iii) the feature ‘II-b’ (‘bright’) that appears brighter than the majority of type-II features in the empty-state image, while slightly dimmer in the filled-state image. Although not shown, we have also observed a bright type-I feature (‘I-b’), which appears to have the same symmetry as the type-I, except with the brightness of the central protrusion in a type-III structure.

The distinction between the various B/Si(001) structures, in particular the type-II and II-b features, becomes more clear when imaged at several different tip-sample bias voltages. Fig. 2.2 shows the result of one such ‘bias-sweep’. While the boron-related structures, as well as the regular Si(001) dimers, show little dependence on the magnitude of the bias voltage in filled-state STM imaging, the variation with bias in empty-state imaging (i.e. positive sample bias) is much stronger. In particular, the type-II feature appears slightly less bright with decreasing positive sample bias voltage, often appearing considerably darker than the surrounding dimers at a sample bias of +1.0V. The type-I structure shows a similar voltage dependence. On the other hand, the II-b structure and the brighter protrusion in the II-bd structure become slightly brighter with decreasing bias voltage.

It should be noted that the appearance and unambiguous identification of these structures depends on the condition of the STM tip. In particular, the type-I structure can be similar in empty-state STM images to the C defect [19] observed by Hamers et al. on Si(001). This defect is marked ‘C’ in Figs. 2.1(a) and (b). However, the ‘bias sweep’ behavior of the type-I distinguishes it from the type C defect, which usually gets brighter with decreasing positive sample bias.
2.3.1.2 Diborane-doped surfaces

Wang et al. [11] reported that exposing undoped Si(001) surfaces to diborane at elevated substrate temperatures resulted in spatial segregation of surface boron into reconstructed patches that either formed islands on top of the surrounding terrace or were incorporated into the otherwise vicinal Si(001) terrace. These structures are distinctly different from the structures discussed above. One might guess that exposing undoped Si(001) to diborane could result in structures distinct from those observed on bulk-doped samples. To test whether the kind of boron-induced structure that form is sensitive to precisely how boron is added to the surface, we have used room temperature STM observations to investigate the atomic-scale structure of surfaces exposed to diborane at elevated temperatures. Our observations show that the structures that form on diborane-exposed surfaces are in fact identical to those observed on bulk boron-doped surfaces. We have found this to be true over almost the entire range of sample temperature (400-800°C) and diborane partial pressure (10^{-9}-10^{-5} Torr) sampled here. For very large diborane pressures, however (~10^{-5} Torr), we sometimes observe structures that resemble those reported by Wang et al. Fig. 2.3 shows a region with a “patchy” reconstructed appearance, which resembles the structures reported by Wang et al. However, the structures shown in Fig. 2.3 are not observed reproducibly, and we have not been able to ascertain whether there is a particular set of experimental parameters for which the Wang-like structures form.
2.3.2 Spatial distribution and temperature dependence of B-structures

Having characterized in detail the various boron-related atomic-scale structures that form, we are now in a position to address the following issues: (1) precisely how might boron reduce the energy cost of creating extra segments of $S_A$-type steps, and (2) what is the origin of the observed temperature-dependence of the striped/finger phase?

Jones et al. [6] observed a striking increase in step density at lower temperatures (< 900 °C), and proposed this was due to temperature-dependent boron surface segregation. Such temperature-dependent segregation has indeed been observed on heavily bulk-doped Si(111) [20]. However, the annealing times in ref. [20] required to obtain equilibrium surface boron concentrations ranged from ½ to 3 hours for temperatures in the 1040-1240K range, significantly longer than typical $S_B$-finger formation times (a few minutes) at similar temperatures. Furthermore, surface segregation on Si(111) surfaces has been shown to be stronger than on Si(001) [21], as well as exhibiting a different functional dependence on temperature. Reported evidence of boron accumulation on heavily bulk-doped Si(001) is restricted to the sublimation regime [12], where preferential Si sublimation is believed to account for the build-up of surface boron. Moreover, reported values of the bulk diffusion coefficient of boron [22] ($D_0=10.5-25$ cm$^2$ s$^{-1}$, $E_a=3.51-3.69$ eV) give diffusion lengths ($\sqrt{Dt}$) ranging from 1 to 5 Å for 2 min anneals at 700 °C. This suggests that, on the time scale of $S_B$-finger formation, the surface boron concentration is not likely to reach its equilibrium value as predicted by classical segregation theory [23]. Nonetheless, the possibility exists that finger formation is accompanied by significant changes in near-surface boron concentration.
To investigate this possibility, we have performed anneal-and-quench STM measurements. Note that comparison with ‘hot’ STM data (i.e., STM performed at elevated temperatures) performed by the research group of Eric Ganz at the University of Minnesota (not shown) shows that the density of type-II structures is not affected by the quench, although our data does not permit us to ascertain whether the quench affects the density of the type-I and -G structures. Investigation of our RT STM data shows that the density of each of the B/Si(001) structures, and thus the overall boron coverage at the surface, is rather insensitive to high temperature processing. This is illustrated in Figs. 2.4(a) and (b), which show filled-state images of a boron-doped Si(001) surface (a) after annealing for 10 min at $T = 700^\circ\text{C}$, and (b) after quenching from the flash at $1250^\circ\text{C}$ directly to room temperature. The insets show that the $700^\circ\text{C}$ annealed sample has well-defined, ordered step fingers, while the $1250^\circ\text{C}$-quenched sample has a lower density of irregularly shaped steps [6]. We quantified the average density and spatial distributions of various boron-related structures on samples annealed at different temperatures, using both filled- and empty-state imaging for more accurate counting.

Fig. 2.4(c) shows the results of such counting for the overall coverage of the type-I, -II, -III, and -G structures. We see that Fig. 2.4(c) does not indicate a significant dependence of the density of surface boron structures on annealing temperature, suggesting that the increased step density observed at lower temperatures may not be due to an increase in the overall surface boron density. As an additional check, we also used Auger Electron Spectroscopy (AES) (Fig. 2.5) to monitor the amount of boron in the near-surface region as a function of annealing temperature. The AES measurements were performed by Hsung-Jai Im in the lab of Jon Pelz at Ohio State University. The amount
of surface boron was quantified by taking the ratio of the B(KLL) Auger peak to the Si(LVV) peak after a sample was annealed for 30 min at a given temperature and then quenched to room temperature. The numbers next to each data point shows the temporal order in which the data were taken. The data in Fig. 2.5 indicate that the near-surface boron coverage is approximately constant for $T < 800 \, ^\circ C$ but then actually increases at higher temperatures. The segregation appears to be largely reversible, provided each anneal is separated by a 1250 °C flash. This behavior is in marked contrast to the behavior reported for boron-doped Si(111) surfaces [20], which shows a decrease in surface boron concentration at higher temperatures. Given the rather slow bulk diffusion of boron at these temperatures, it is possible that the segregation behavior seen in Fig. 2.5 is kinetically limited, and does not represent equilibrium behavior. We also note that the behavior in Fig. 2.5 appears to disagree with our STM observations, which indicate a roughly constant density of B structures for different annealing conditions. Since the information depth of Auger electrons (at ~3 keV) extends over several monolayers, it is possible that the surface boron coverage (as observed by STM) may be roughly constant, while the boron concentration in lower layers varies with annealing temperature.

Jones et al. suggested that preferential boron segregation to the $S_A$-step edges could decrease the $S_A$-step creation energy, thereby providing a possible mechanism for enhancing step formation. We have indeed found that the type-II feature is more than twice as likely to occupy a site at the lower edge of $S_A$-steps than on the surrounding terrace. Overall, we have found that the type-II structure prefers $S_A$-step edge sites to terrace sites by a ratio of $2.39 \pm .15$. However, this tendency of the type-II features to stick to $S_A$-step edges does not appear to change systematically with annealing
2.3.3 Controlled stripe formation on ultra-flat Si(001) surfaces

Studies of striped phase formation on boron-doped Si(001)-(2×1) have so far been mostly limited to vicinal surfaces, on which pre-existing steps must be present due to a finite surface miscut away from the [001] crystal direction. In this case, step creation generally occurs by a spontaneous lengthening of pre-existing step-edges, rather than the nucleation of entirely new islands and/or pits. The maximum size of a striped “domain” is hence limited by the pre-existing steps, which also affect the size and shape of the step patterns that develop [24]. We now explore spontaneous step creation on initially step-free surfaces, where step creation is unhindered by pre-existing steps. Our goal is to understand the factors that control the large-scale patterns that develop, and to create large (>5 µm) single-domain arrangements of long step stripes, with all stripes over a large area oriented in the same direction. This could be of potential use as a spontaneously-formed step grating, with a step spacing that can be dynamically tuned by varying sample temperature and/or surface boron content.

Here we report real-time low-energy electron microscopy (LEEM) observations of ultra-flat Si(001) surfaces exposed to diborane at elevated temperatures. This allows us to add controlled amounts of boron to large, step-free areas on the surface, and hence to observe the formation of boron-induced step structures without the influence of vicinal surface steps. For a wide range of boron deposition conditions, we find that the step creation process is kinetically limited, and is strongly influenced by the availability of
free surface Si atoms. This leads to the formation of *multiple-domain* stripe patterns on large terraces, with each domain limited to ~1 µm in size. However, by depositing ~½ ML of extra Si atoms prior to diborane exposure, it is possible to foster the formation of very large (>5 µm) single-domain stripe patterns.

Fig. 2.6(a) shows a ~6 µm step-free terrace prior to B$_2$H$_6$ exposure, while Fig. 2.6(b)-(e) show the same terrace as it is dosed with ~10$^{-7}$ Torr B$_2$H$_6$ at 740°C during a ~12 min time period. The method by which large step-free terraces were prepared will be discussed in detail in Chapter 4. The dimer row direction on the large terrace is indicated by the arrow in the upper right-hand corner in Fig. 2.6(a). Initially, step fingers begin to grow onto the terrace from the crater walls, as shown in Fig. 2.6(b). This finger growth from existing step-edges is similar to what occurs on vicinal surfaces [6]. However, we also observe in Fig. 2.6(b) the formation of elongated ML-deep *pits* on parts of the terrace far from the crater walls (indicated by the arrow in 1(b)), followed by formation of isolated *islands* (arrow in 1(c)) located close to the pits. We can distinguish whether an isolated structure is an island (1 ML above the surrounding terrace) or a pit (1 ML below) by its elongation with respect to the fingers at the crater wall. Due to the difference in the S$_A$- and S$_B$-type step energies, ML-high islands (pits) are elongated perpendicular (parallel) to the dimer rows on the surrounding terraces [25].

The isolated island in Fig. 2.6(b) evolved into one of several “island domains” (arrow in Fig. 2.6(e)), *i.e.*, rectangular regions consisting of a collection of long thin islands, each of which is a single stripe about ~10 - 15 nm wide. We cannot resolve these individual stripes in Fig. 2.6(e), but have confirmed they exist from atomic force microscope (AFM) images of similarly prepared samples after removal from UHV, as
shown in Fig. 2.6(f). We also observe that the regions around the island domains become finely striped as well, but are (on average) 1 ML lower than the island domains and consist of fine stripes oriented perpendicular to the stripes on island domains. We shall call these areas “terrace domains”. Hence the initially step-free 6 µm terrace has evolved into a multi-domain arrangement of striped regions, with the lateral size of each domain much smaller than the initial flat terrace.

To investigate whether the kinetics of the step formation process is responsible for this multi-domain structure, we have performed similar experiments using different B$_2$H$_6$ pressure. Fig. 2.7 shows such a sequence of LEEM measurements at 740°C, but with ~10^-6 Torr B$_2$H$_6$. The initial finger formation at the crater walls appears similar to the 10^-7 Torr case shown in Fig. 2.7, but the sequence of domain formation away from the crater walls is different. In particular, isolated islands are first observed out on the terrace (arrow in Fig. Fig. 2.7(a)), followed closely by the formation of nearby pits. In this case the terrace also evolves into a multi-domain, finely-striped structure, but in this case the island domains are significantly thinner and more elongated than for the 10^-7 Torr B$_2$H$_6$ case. It is clear that the kinetics of the domain formation process is very important.

We propose that the terraces form a multi-domain structure because of a limited supply of free Si adatoms away from the crater walls. Consider the formation of an island domain on an initially step-free terrace. Two surface levels are present on an island domain: the original terrace level (designated “level 0”) and the level on top of the stripes (“level 1”). Hence to form such an island domain, it is necessary to add ~½ ML of Si to this part of the surface. In contrast, formation of terrace domains (which expose level 0 and level −1) necessarily requires the local removal of ~½ ML of Si. Since
adatoms can easily detach from existing step-edges, there is a ready supply of extra Si adatoms close to the crater walls. For this reason, step fingers can easily and quickly form close to the crater walls (see Fig. 2.6(b) and Fig. 2.7(a)). However, free Si adatoms are in short supply on areas far from the crater walls, so in these regions *island domains can only form in conjunction with the formation of nearby terrace domains*. In effect, the ~½ ML of Si necessary for the island domains to form is supplied by the ~½ ML of Si that is freed when the terrace domains form. This is very likely the reason why newly formed islands tend to be “decorated” by newly formed nearby pits, as illustrated in Fig. 2.7(b).

If this explanation for multi-domain formation is correct, then we should be able to foster large, single-domain formation by supplying ½ ML of Si to the surface from an external source. Fig. 2.8 shows the successful results of such an experiment. Prior to B\(_2\)H\(_6\) exposure, we deposited ~½ ML of Si onto the initially step-free terrace, resulting in large Si islands covering ~½ of the crater, as shown in Fig. 2.8(a). The sample was then exposed to B\(_2\)H\(_6\), leading to finger- and island formation over most of the surface. Since extra Si is already present over most of the crater, very few pits form. After adding a small amount of additional Si, as well as exposing the surface to relatively small doses of diborane (Fig. 2.8(b)-(d)), most of the terrace indeed becomes covered with a single-domain striped phase, with only two surface levels present. Hence, with care and an external source of Si atoms, it is possible to use the boron-Si(001) system to produce large (~ 5μm), self-assembled, single-domain stripe gratings with adjustable step density.
In summary, we have shown that the formation of a striped phase during diborane exposure of ultra-flat Si(001) terraces is limited by the supply of free Si adatoms, leading to the formation of multi-domain step structures if no external source of Si atoms is available. With controlled deposition of extra Si atoms, it is possible to produce uniform single-domain striped structures over large areas.

2.4 Summary

Several novel boron-induced structures have been characterized. The type-II structure was found to decorate $S_A$-type step edges, offering a possible mechanism for step energy lowering. However, high-temperature annealing does not affect the density or location of any of the B/Si(001) structures as measured by STM, leaving unresolved the temperature dependence of the $S_B$-step finger density. On initially step-free surfaces, the formation of new surface steps during diborane exposure is limited by the supply of diffusing addimers. By preparing the surface to allow for a large supply of surface atoms, single-domain striped terraces can be formed in a controlled manner.
Fig 2.1. RT filled (a, c, e) and empty (b, d, f) state STM images of boron-doped Si(001) [±1.8 V, 1.0 nA, scan size 100 Å (a and b) and 400 Å (c-f)]. The most common structure is the type ‘II’, followed by the type ‘I’, the type ‘G’, and finally the type ‘III’. The ‘II-1w’, ‘II-b’, and ‘II-bd’ structures are variations on the type-II structure (see text). A type C defect (not B-related) is shown for comparison with the type-I structure.
Fig 2.2. RT STM ‘Bias sweep’ of boron-doped Si(001) [1.0 nA, scan size 100 Å]. The sample bias for each image is shown. While the type-II structure nearly disappears at low positive sample bias voltage (empty state imaging), the bright type-II-b structure grows slightly brighter with decreasing voltage. The brighter protrusion in the ‘II-bd’ structure (see text) appears similar to a type-II-b protrusion. The appearance in filled-state imaging is nearly independent of the magnitude of the bias voltage (not shown).
Fig 2.3. STM images of a Si(001) surface exposed to high diborane pressures (10^{-6} Torr) at 530°C. The observed structures are similar to those reported by Wang et al. However, the structures shown are not observed reproducibly, and in most cases, only the Kulakov-like structures are observed.
Fig 2.4. (a) RT STM scan [$V_{\text{sample}} = -1.8 \, \text{V}, \, 1.0 \, \text{nA}, \, \text{scan size} \, 400 \, \text{Å}$] taken after a 700°C anneal. (b) RT STM scan [$V_{\text{sample}} = -1.8 \, \text{V}, \, 1.0 \, \text{nA}, \, \text{scan size} \, 400 \, \text{Å}$] taken after the sample was quenched from flash temperature to RT. Insets [$V_{\text{sample}} = -1.8 \, \text{V}, \, \text{scan size} \, 5000 \, \text{Å}$] show the large-scale morphology in each case. (c) Densities of the various B-related structures obtained from STM images. After a flash at 1250 °C, the samples underwent one of three high-temperature processes: (i) a 600 °C anneal followed by a quench to RT, (ii) a 700 °C anneal followed by a quench to RT, and (iii) a quench to RT from flash temperature. The data points for these processes are shown at temperatures 600 °C, 700 °C, and 1250 °C, respectively. The ML coverage for each structure was obtained by dividing the densities of each structure by the density of Si(001) lattice sites ($6.78 \times 10^{-14} \, \text{cm}^{-2}$).
Fig 2.5. Auger data of annealed, heavily boron-doped Si(001). The ratio of the B $KLL$ to Si $LVV$ peaks is plotted against annealing temperature. The numbers attached to each data point label the temporal order in which the data were taken. Error bars represent experimental uncertainty due to noise in Auger signal. Inset: representative Auger spectrum.
Fig 2.6. (a-e) Sequence of LEEM images of an initially step-free Si(001) terrace during diborane exposure at $10^{-7}$ Torr, with the sample held at 740°C. (a) Large, step-free terrace (dark area) prior to diborane exposure. The arrow indicates the terrace dimer-row direction. (b-e) Same area after 475 s, 515 s, 635 s, and 745 s of diborane exposure, respectively. Arrow in (b), (c), and (d) indicates a new pit, a new island, and an “island domain”, respectively (see text). (f) AFM close-up of an island domain on a similarly prepared boron-doped Si(001) surface.
Fig 2.7. Similar LEEM sequence as in Fig. 2.6, except for a diborane pressure of $10^{-6}$ Torr at 740°C. (a-d) Step-free terrace after 115 s, 130 s, 140 s, and 160 s diborane exposure, respectively. Arrow in (a) indicates a new island.
Fig 2.8. LEEM sequence showing formation of a “single-domain” striped phase covering most of the $6 \times 6 \, \mu\text{m}^2$ crater. (a) Step-free terrace after deposition of $\sim \frac{1}{2}$ ML of Si, but prior to diborane exposure. (b-d) Evolution of same area during several cycles of diborane exposure, additional Si deposition, and annealing at 740$^\circ$C.
CHAPTER 3

STEP REARRANGEMENT AND SURFACE MASS TRANSPORT ON SILICON SURFACES HEATED WITH DIRECT CURRENT

3.1 Introduction

In the past decade, much experimental and theoretical work in the field of crystal surface dynamics under non-equilibrium conditions has focused on characterizing and understanding the morphology of crystals heated with direct current (DC) to sublimation temperatures. The interest in such surface “electromigration” effects stems not only from a desire to characterize fundamental atomic processes on evaporating crystals, but is also motivated by the need to understand and control electromigration-induced breakdown of metal interconnects in semiconductor devices. The pioneering work on electromigration effects on silicon surfaces was done by Latyshev et al. [26], who observed that DC heating of a silicon wafer to high temperatures could produce large-scale “step bunching”. Since then, surface electromigration instabilities on Si have been extensively studied, particularly for vicinal Si(111) surfaces [27,28].
Most prior studies of surface electromigration phenomena on Si surfaces have focused on conditions in which the applied current is *perpendicular* to the step direction on the “pristine” surface (before annealing). Here I will discuss surface electromigration experiments on Si(001) and Si(111) surfaces, with a particular emphasis on how these phenomena depend on the *direction* of the applied DC current with respect to (1) the local miscut (both magnitude and direction) and (2) the direction of the Si(001)-(2×1) surface dimer rows. For this purpose, we have used Si(001) and Si(111) samples in which we have ground spherical “dimples” (~76 mm radius) with local miscut ranging from ~0° – ±1°. The resulting surface morphology is found to depend strongly on current direction with respect to (1) the local miscut direction, and (2) the direction of the Si(001) dimer rows. In particular, we have found that the orientation (with respect to the applied current direction) of the various step structures that form on the dimple “rotate” by 90° when the current direction is rotated by 45° away from a <110> direction. We argue that this behavior suggests that the force exerted by the applied DC field on a diffusing adparticle can be parallel, anti-parallel, or even *sideways* to the applied field, depending on the angle between the applied field and the [110] direction. We have also observed a novel “step bending” instability [35] on Si(001) surfaces, which is expected to occur on parts of the dimple where the surface mass flow is roughly *parallel* to steps on the pristine surface. This step bending instability has been predicted theoretically [35], but has not been previously observed.
3.2 Background information

Since the initial reports by Latyshev et al., it has been known that DC heating of Si(111) or Si(001) samples at high temperatures (\( > 900^\circ C \)) can produce a variety of large scale surface structures. These surface electromigration phenomena are thought to arise from a directional drift of surface atoms, which can produce a variety of instabilities in the underlying step structure on vicinal Si surfaces. Step bunching is the best known of these instabilities [26-31] and leads to the formation of bunches of steps (up to several hundred in a bunch) separated by terraces up to several \( \mu \text{m} \) wide. There are also experimental reports and theoretical modeling of "step wandering" [32-34,44] and step bending [35]. Step bunching and wandering are both expected to occur on areas of the sample where surface atoms have a component of their drift velocity that is perpendicular to the average step direction, whereas step bending is predicted to occur when the drift velocity is parallel to the average step direction.

On Si(111) it is well known that, for a given temperature and sublimation/growth condition, step bunching only occurs for one “sense” (either step-up or step-down) of the applied current, but not for both senses under a particular annealing condition. Here step-up (step-down) current means that the applied direct current has a component pointing up-hill (down-hill) with respect to the staircase of steps on the vicinal surface. Surprisingly, the sense of the applied current that produces step bunching on Si(111) can change several times with increasing temperature [26,27] and/or the sublimation/growth conditions of the sample during DC annealing [30]. We note that two leading models for
surface electromigration on Si both predict that bunching should only occur for one sense of the adatom drift direction for a given annealing condition [36-40].

Surface electromigration behavior on the Si(001)-(2\times1) surface is different in two important ways. Firstly, step bunching has been reported for both step-up and step-down current at the same temperature [41-44], at least for temperatures in the range 950-1150°C. Secondly, DC annealing at high temperatures generally causes adjacent steps to pair or “couple”. Latyshev [45] was the first to observe that on Si(001) samples heated at high temperatures by a DC current directed along a \langle110\rangle direction, adjacent steps couple in such a way that terraces with one of the dimer row directions becomes dominant. The majority dimer row direction is parallel (perpendicular) to the applied current for step-down (step-up) current. This coupling persists as the steps bunch, so that bunches generally consist of an even number of single-layer steps, with the same dominant dimer row direction on both sides of a bunch. This step coupling is direct evidence of anisotropic DC-induced surface mass flow [46], and will be discussed in more detail later.

### 3.3 Experiment

The samples studied in this report were lightly phosphorus-doped Si(001) (nominal resistivity .08-.3 Ω-cm) and Si(111) (.075-.2 Ω-cm) wafers. The Si(001) samples were cut into rectangular pieces (of typical dimension 15 mm \times 3 mm \times .5 mm), with the long axis of the rectangle oriented along the [\bar{T}10] or [010] crystal direction. The long end of the Si(111) samples were oriented along a \langle1\bar{1}0\rangle direction. Spherical dimples of 76
mm radius were then mechanically ground near the middle of the samples using a 1 µm diamond compound, followed by chemi-mechanical polishing using a colloidal silica suspension. The dimples were typically 2-3 mm across, resulting in a nominal miscut ranging from –1° to +1° across the dimple. Before introduction into the UHV chamber, samples underwent an ultrasonic clean (trichloroethylene → acetone → methanol, 5 min each) and/or a UV-ozone clean. Previous studies in our group [47] using this procedure on Si(001) surfaces with a smaller radius (8 mm) grinding wheel have been shown to produce surfaces of varying miscut with low atomic-defect density once the samples are flashed at 1250°C inside our UHV chamber.

Electrical contacts were attached at the two ends of the sample, and heating was done by passing an electric current (either DC or AC) through the sample. Once inside the UHV chamber (base pressure < 2×10^{-10} Torr), samples were degassed at 750°C for 6 hours and flashed several times at 1250°C to produce a clean surface. The samples were then heated with direct current (~5 A, 8 V/cm) along the long axis of the rectangular sample to 990°C or higher for 1/2 - 32 hours, then quenched to room temperature. Although the chamber pressure remained low during quick flashes, it could rise to as high as 5×10^{-9} Torr during extended annealing. This is of potential concern, since earlier STM studies [48] indicate that poor UHV conditions can lead to the formation of nm-sized particulates (thought to be SiC) which can "pin" surface steps. Since we observe few such pinning sites on our annealed surfaces, we conclude that this kind of surface contamination is not a serious problem for the work presented here. However, we cannot rule out the possibility that this higher background pressure (mostly H₂) during extended
annealing could affect the mobility and/or the sublimation rate of surface atoms. After annealing, samples were removed from UHV and studied with "tapping-mode" atomic force microscopy (AFM) and with optical microscopy.

3.4 Results

3.4.1 Si(111)

Fig. 3.1 shows a dimpled Si(111) surface after annealing at 1200°C for 30 minutes with the applied DC current directed upward in the image. Fig. 3.1 (a) shows a large-scale optical micrograph of the area near the bottom of the dimple (marked “x”). Due to the spherical geometry of the dimple, the applied electric field (and hence the applied bulk current) is directed in a step-down (step-up) direction below (above) the center of the dimple as viewed in the figure, whereas the applied current is directed parallel to the steps on the sides of the dimple center.

Figs. 3.1(b)-(d) show AFM close-up views of the regions above, to the side of, and below the center of the dimple, respectively. All images are shown in “derivative mode” (DM), with the gray-scale keyed to the derivative of the surface along the scan direction. The AFM images in Figs. 3.1(b) and (d) should be viewed as if illuminated from the top, whereas the image in Fig. 3.1(c) should be viewed as if illuminated from the left. Fig. 3.1(b) shows an area of the sample where the applied current is directed in a step-up direction, and reveals large-scale step bunching behavior. The step bunches appear as wide, dark bands in the figure. We also observe a number of single-height “crossing steps” [49-51] on the terraces separating the step bunches, which appear as the thin, dark
lines in the image. On the side of the dimple (Fig. 3.1(c)), where the direction of the applied current is parallel to the average step direction, we observe no obvious signs of a step instability. Fig. 3.1(d) shows an area where the applied current is directed in a step-down direction, and reveals a vicinal surface (a regular train of single-layer steps) with no obvious signs of bunching or any other step instability. Hence, we see from Fig. 1 that step bunching on Si(111) occurs for only one sense of the applied current under a given annealing condition, consistent with the behavior reported in other studies [26-31].

3.4.2 Si(001)

3.4.2.1 Current along <110>

The behavior on dimpled Si(001) surfaces is much more complex. Fig. 3.2 shows a typical dimpled Si(001) sample after annealing at 990°C for 18 hrs with the applied direct current directed toward the [110] crystal direction, which is upward in the image as shown. Fig. 3.2 (a) shows a large-scale optical micrograph of the area near the bottom of the dimple (marked "x"), while Figs. 3.2(b) and 3.2(c) show AFM close-up views of the dotted regions in Fig. 3.2(a). Figs. 3.2(b) and 3.2(c) reveal large step-bunches (~100 steps per bunch) for both step-up (Fig. 3.2(b)) and step-down (Fig. 3.2(c)) current, consistent with previous reports [41-44]. The wide terraces between the step bunches are decorated by crossing steps, which appear similar in appearance to electromigration-induced crossing steps reported on the Si(111) surface [49-51] and observed in Fig. 3.1(b). However, it is important to note that nearly all of the crossing steps observed in Fig. 3.2(c), and to a lesser extent those in Fig. 3.2(b), are in fact coupled steps. Hence, the dimer row direction is the same on both sides of a coupled crossing step. The dimer row
orientation on the terraces between the step bunches was determined from AFM close-up images (not shown) by observing the orientation of elliptical vacancy pits that are sometimes observed on wide terraces. The equilibrium shape of vacancy pits (islands) on Si(001) is known [52,53] to be elliptical, with the major axis of a vacancy pit (island) oriented parallel (perpendicular) to the dimer rows on the surrounding terrace. We find that the dimer rows on the majority terrace run parallel to the applied current direction on areas of the sample where the applied current is step-down (over most of the bottom half of the dimple as viewed in Fig. 3.2), while the majority-terrace dimer rows are perpendicular to the applied current on areas where the current is step-up (on the top half of the dimple). These observations are consistent with prior reports of step coupling on Si(001) when current is applied along a <110> crystal direction [3], and is observed on all of our dimpled samples in which the current is applied along a <110> direction.

We also note that above the center of the dimple, step bunched regions are sometimes observed to coexist side-by-side with step wandering patterns [32-34,44], which appear as the vertical grooves near the top of Fig. 3.2(a). This step wandering phase consists of sinusoidal step undulations that have an in-phase relation on adjacent terraces [33,34], which produce μm-scale grooves in the surface morphology that have an approximately sinusoidal cross section. Fig. 3.3(a) shows an AFM scan of a similar step wandering pattern from another sample (which was annealed at 1040°C for 32 hours with the applied current directed toward the [101] direction), while Fig. 3.3(b) shows a cross-section across several grooves. As can be seen in Fig. 3.2(a), the grooves are oriented along [101] for a range of azimuthal angles around the dimple center, and hence do not
form a radial pattern pointing toward the dimple center. We have observed such step wandering patterns only in areas where the applied current has a step-up component, and only for relatively low miscut angles (< 0.5°). We note here that these observations are somewhat different from those of Degawa et al. [32] and Nishimura et al. [44], who observed wandering patterns i) for step-down current along the [211] crystal direction on Si(111) samples heated to 1100-1200°C for 24 hours, and ii) at high miscut angles (13-14°) on Si(001) samples heated to 1000-1200°C for 7-100 hours with step-down current along a <100> crystal direction.

We also note that some Si(001) samples heated with direct current in the [101] crystal direction show a qualitatively different behavior from that seen in Fig. 3.2, even under nominally identical conditions (i.e. substrate temperature and duration of anneal). Fig. 3.4 shows an example of a dimpled sample exhibiting this alternate behavior. Fig. 3.4(a) shows a large-scale optical image of the dimple, and Figs. 3.4(b) and 3.4(c) show AFM close-up views of the dotted regions in Fig. 3.4(a). As in Fig. 3.2, the sample shown in Fig. 3.4 exhibits step bunching at both the top and bottom of the dimple. However, no step wandering patterns are observed in this case. Furthermore, the sides of the dimple (where the applied DC current is approximately parallel to the average step direction) reveal what we believe to be a qualitatively different step bending pattern [35], which has been predicted to occur when the applied current is parallel to the average step direction [35]. These step structures appear as parallel bands oriented roughly 45° to the direction of the applied current, and will be discussed in more detail below.
We also see that the step bunches in Fig. 3.4 appear somewhat different for step-down and step-up current: for step-up current (Fig. 3.4(b)), the bunches are quite steep (~1°) and straight, whereas for step-down current (Fig. 3.4(c)), the bunches are more irregular and of moderate slope (~1-1°). Furthermore, the step coupling is stronger (i.e. the coupled steps are closer together) for current in the step-up direction. Curiously, on samples exhibiting behavior similar to that shown in Fig. 3.2, the situation is roughly reversed, with weaker step coupling and more irregular and moderately sloped bunches on the step-up half of the dimple.

Although there is some variability in the details of the step bunching on different samples, it is important to note that nearly all samples show bunching for both step-up and step-down current (on 2 out of 13 dimpled samples investigated, the step wandering pattern covered most of the step-up side of the dimple, with little step bunching observed on that side). As noted earlier, this is distinctly different from the behavior seen on Si(111), where bunching is observed for only one sense of the applied current. This behavior, which has been a long-standing puzzle, will be discussed further below.

We have also done tests where annealing was done using alternating current (AC). In this case, we observe no step instabilities, in agreement with previous reports [32,42]. We therefore believe that the observed step bunching cannot result from a simple “Erlich-Schwoebel Barrier” (ESB) effect [54-57], as has been recently suggested [44]. An ESB refers to an energy barrier for adatom attachment/detachment to a step, which may be different for adatom exchange with the upper terrace as compared to the lower terrace. A larger attachment/detachment barrier for adatom exchange with the upper terrace could lead to step bunching under conditions of net sublimation. However, this mechanism (if
present) should not depend on whether AC, DC, or indirect sample heating is used. Since AC heating produces no step bunching, we do not believe a simple ESB effect can be the origin of the observed step bunching on Si(001). Furthermore, Fig. 3.2 clearly shows that the direction of the applied direct current imposes a definite symmetry on the step bunching patterns: the bunching is strongest where the applied current is oriented perpendicular to the local step direction. If a simple ESB were responsible for the bunching, one would expect the bunching to be insensitive to the direction of the applied current with respect to the local step direction. Fig. 3.2 shows that this is clearly not the case.

3.4.2.2 Current along <100>

We have also investigated Si(001) surfaces with the DC heating current applied in the [010] direction, so that the applied current flows at 45° to the surface dimer rows. In this case we observe surprising and dramatically different step coupling and step bunching patterns. Fig. 3.5(a) shows an optical micrograph of a dimpled Si(001) surface after annealing at 1040°C for 18 hrs with the applied current directed upward in the image, along the [010] crystal direction. Remarkably, the step bunching pattern appears to have rotated ~90° compared to the bunching pattern observed when the applied current is in the [1̅1̅0] direction. In Fig. 3.5, the bunching is most pronounced directly off to the sides of the dimple center, where the applied current is roughly parallel to the local step orientation. The bunching is in fact weakest near the top and bottom parts of the dimple, where the applied current is mostly perpendicular to the steps. This is nearly opposite to the behavior observed when the applied current is parallel to [1̅1̅0] (see Figs. 3.2 and
3.4), where bunching is strongest where the applied current is mostly perpendicular to the step edges. This surprising step bunching behavior on Si(001) for applied current in the [010] direction has not been previously reported.

Figs. 3.5(b) and 3.5(c) show AFM close-up views of the step-bunched areas off to the left and right of the center of the dimple, respectively. The bunching and the appearance of the crossing steps appear qualitatively similar to those in Figs. 3.2 and 3.4, where the current is applied along the [101] direction. As in Figs. 3.2 and 3.4, the crossing steps in Figs. 3.5(b) and 3.5(c) turn out to be coupled steps. AFM close-up images of small pits on the terraces between the step bunches indicate that the coupling is such that the dimer rows on the majority terrace on the left-hand side of the dimple run from the lower left-hand corner to the upper right-hand corner, whereas the dimer rows on the majority terrace on the right-hand side of the dimple run from the lower right-hand corner to the upper left-hand corner. The parallel lines in the figure indicate the dimer row direction on the majority terrace. Hence, rather than the “top-bottom” contrast in the step coupling that is observed when the heating current is applied along the [101] crystal direction, the coupling on surfaces where the current is applied along the [010] crystal direction shows a “left-right” contrast. We will return to the origin of this step coupling in the next section of the paper. We also note that the appearance of the step bunches and the crossing steps are similar on the left- and right-hand sides of the dimple.

3.4.2.3 Summary of step bunching and coupling behavior on Si(001)

Figs. 3.6(a) and 3.6(b) summarize our observations of step bunching and step coupling on Si(001). The figures show schematic views of a dimple and the observed step
bunching and coupling when the heating current is applied along the (a) \([\bar{1}10]\) and (b) \([010]\) crystal directions. The heavy arced bands represent the observed step bunching patterns, the outer dashed line represents the perimeter of the dimple, and the thin straight lines indicate the dimer row direction on the majority terraces. For clarity, the coupled crossing steps are not shown on this schematic figure. The straight, dashed “transition line” in Figs. 3.6(a) and 3.6(b) indicate regions of the dimple where the step bunching disappears or changes qualitative form. This transition region for the bunching appears to coincide with the region where the coupling “switches”, i.e. where the majority domain changes from \((2\times1)\) to \((1\times2)\). As shown in Figs. 3.6(a) and 3.6(b), direct current heating along the \([\bar{1}10]\) \(([010]\)) direction results in a top-bottom (left-right) contrast in both the coupling and the bunching patterns.

**3.4.3 Step bending instability on Si(001)**

Before analyzing in detail the behavior in Figs. 3.6(a) and 3.6(b), I will discuss in some detail the novel step structure observed on the sides of the dimple in Fig. 3.4(a). Fig. 3.7 shows a composite AFM image of another sample showing similar step bending patterns directly off to the sides of the dimple center. The sample in Fig. 3.7 was annealed for 4.5 hours at 1040°C. Note that the current direction is down in this image. Step bunched areas are seen both near the top (step-down current) and bottom (step-up current) of the composite image. On the right-hand side of the dimple we again observe bands running roughly 45° to the direction of the applied current.
The middle image in Fig. 3.7 is shown again in Fig. 3.8(a), and AFM close-up views of the boxed areas in Fig. 3.8(a) are shown in Figs. 3.8(b) and (c). We see from Fig. 3.8(a) that this step pattern consists of “wavy” undulations of the individual steps which have a non-zero phase relationship between adjacent steps. The waviness of the individual steps is apparent in the region pointed to by the arrow in Fig. 3.8(c), which shows successive steps assuming undulations of increasing amplitude. To verify that these steps were initially parallel to the applied current direction, we have measured the height of the bands with high step density and the density of the (paired) steps on the terraces between the step bands. The average miscut over the entire area shown in Fig. 4(b) was found to be \( \sim 0.08^\circ \) (which is the value one would expect at a distance \( \sim 100 \mu m \) from the bottom of a 75 mm radius spherical dimple) pointing directly to the left (toward the bottom of the dimple). Hence we conclude that the steps in this sample region were indeed running parallel to the current direction on the pristine surface. Fig. 3.8(d) illustrates how sinusoidal step undulations with a non-zero phase relationship give rise to “bands” of high step density (running at an oblique angle to the initial step direction) separated by regions of relatively low step density.

### 3.4.3.1 Comparison with theory

The step patterns presented in Fig. 3.8 are remarkably similar to the step bending instability predicted by Liu et al. [35], which was predicted to occur when the current direction is parallel to the steps on the pristine surface.

In this case, Liu et al. predicted that steps would form undulations with a definite non-zero phase shift between them, in such a way that surface “bands” would appear
which alternate between a narrow and wide spacing between adjacent steps. This step bending instability is distinct from both normal step-bunching (with no lateral undulations) and step wandering (in-phase, zero-degree phase shift). For step bending, the maximum instability is expected for undulations with adjacent steps $\pi/2$ out of phase, resulting in bands of high step density running at an angle to both the average step direction and the direction of the applied current. The step structures shown in Fig. 3.8 are particularly similar to the theoretical simulations of the step bending instability done by Liu et al., as shown in Fig. 4 from Ref. [35]. Based on the striking similarity of the observations presented here with the predictions by Liu et al., we believe the structures shown in Fig. 3.8 represent the first observations of a step bending instability.

According to Liu et al., the sense of the out-of-phase step undulations is determined by the direction of the externally applied force on the adatoms. To produce bands of high step density running from the lower left-hand corner toward the upper right-hand corner in Fig. 3.8(d), their model – which assumes a diffusion bias parallel to the average step direction and the presence of a step attachment barrier – requires a net drift of adatoms that would be upward in the figure. This would suggest that the force acting on the surface adatoms in Figs. 3(b) and (c) is directed upward in these images, i.e. opposite to the direction of the applied current. We note here that this is opposite to the assumptions made in past studies of step pairing [45] and island drift [58]. This apparent contradiction is addressed below.

While no strong signs of a step bending pattern were observed on the Si(111) samples studied here, it is interesting to note that the steps in Fig. 3.1(c) do appear to take on slightly wavelike undulations. It is possible that a step bending instability may be
realized in a more striking manner if the sample is annealed significantly longer. In fact, the relatively short annealing times used in this study could also account for why we are not able to reproduce the observations of Degawa et al. [32], who observed step wandering patterns for step-down current on Si(111) samples annealed under similar conditions for 24 hours. Although the steps in Fig. 3.1(d) do in fact exhibit slight in-phase wavy undulations (which is the signature of a wandering instability), we have not yet studied whether these evolve into step-wandering patterns for longer annealing times.

3.5 Analysis: anisotropy of surface mass transport on Si(001)

To analyze the significance of the observations in Figs. 3.6(a) and 3.6(b) in more detail, we now consider formally how the surface mass flow and the resulting coupling and/or bunching depends on the direction of the applied current with respect to the surface dimer row direction, and to the local step direction.

3.5.1 Formalism

The notation we will use is illustrated in Fig. 3.9(a), which shows a schematic view of a dimpled Si(001) surface before annealing (before any step coupling or bunching has taken place), and Fig. 3.9(b) shows a more detailed view of the boxed region in Fig. 3.9(a). We choose a coordinate system such that the x- and y-axes are parallel to the [110] and [\Bar{1}10] crystal directions, respectively, as shown in the figure. In order to compare with the experimental results summarized in Figs. 3.6(a) and 3.6(b), we assume the applied current $\vec{I}$ (and hence the applied electric field $\vec{E}$) is directed vertically upward.
in the figure. We define $\phi$ as the angle between $\vec{E}$ and the local “step-normal” $\vec{n}$, the unit vector orthogonal to the (local) step direction and pointing towards the upper terrace. For a dimple with circular symmetry, $\phi$ is equal to the azimuthal angle around the dimple center referenced to the vertical ($+\vec{E}$) direction, as shown in Fig. 3.9(a). In our experiments, we can vary $\phi$ simply by looking at different locations around the dimple.

We define $\theta$ as the angle from $\vec{E}$ to the $[\overline{1}0\overline{1}]$ crystal direction. Experimentally, $\vec{I}$ and $\vec{E}$ are parallel to the long axis of the rectangular Si wafer, so $\theta$ is fixed by how the Si sample is cut with respect to the Si crystal directions. With respect to the coordinate system defined in Fig. 3.9, $\vec{E} = E[\sin(\theta)\hat{x} + \cos(\theta)\hat{y}]$ (where $E$ is the magnitude of $\vec{E}$) and $\vec{n} = \sin(\theta - \phi)\hat{x} + \cos(\theta - \phi)\hat{y}$. We also define a “type-1” or “type-2” terrace as a terrace on which the dimer rows run parallel or perpendicular to the $[110]$ crystal direction, respectively. We further define an $S_1$ or $S_2$ step as a step bounded on its upper side by a type-1 terrace or type-2 terrace, respectively.

We next consider the flow of surface atoms due to the applied current. Here, we generally follow the assumptions and approach of Latyshev [45] and Stoyanov [46], who studied coupling of steps on Si(001)-(2×1) surfaces during DC heating, as well as work by Métois et al. [58], who studied the DC-induced motion of Si islands on Si(001). These authors assumed the direct current in the Si sample cause the diffusing surface species (which we generically refer to here as an “adparticle”) to develop an average drift velocity

$$\vec{v}_{\text{drift}} = \vec{F} - \frac{D}{k_B T}$$

(1)
where $\vec{F}$ is the net force acting on the adparticle, $D$ is the adparticle diffusion constant, $k_B$ is the Boltzmann constant, and $T$ is the temperature. In electromigration studies, the force $\vec{F}$ is often related to the electric field $\vec{E}$ in the sample by $\vec{F} = q_{\text{eff}} \vec{E}$, where $q_{\text{eff}}$ is the “effective charge” of the adparticle [31,59]. The net force $\vec{F}$ is generally thought to be the sum of two parts [59]: a “direct” electrostatic force $\vec{F}_{\text{direct}} = q_{\text{direct}} \vec{E}$ (where $q_{\text{direct}}$ is the actual electrostatic charge of the adparticle) and an “electron wind” force $\vec{F}_{\text{wind}} = q_{\text{wind}} \vec{E}$ due to momentum-transfer from drifting electrons at the sample surface. Note that $q_{\text{wind}}$ does not represent an actual charge, but rather is a convenient parameter for relating $\vec{F}_{\text{wind}}$ to $\vec{E}$. With these definitions, $q_{\text{eff}} = q_{\text{direct}} + q_{\text{wind}}$. Past studies [59] have generally treated $q_{\text{wind}}$ as a scalar quantity with negative sign (since electrons generally drift opposite to $\vec{E}$), and have pointed out that $q_{\text{eff}}$ could be positive or negative depending on the sign of $q_{\text{direct}}$ and the relative magnitudes of $q_{\text{wind}}$ and $q_{\text{direct}}$.

Previous authors considered step coupling [46] and island drift [58] on Si(001) surfaces only for situations when $\vec{E}$ was along a high-symmetry $<110>$ crystal direction ($\theta = 0$) and for steps that were perpendicular to $\vec{E}$ ($\phi = 0$). Here, we consider the more general situation with arbitrary $\theta$ and $\phi$. The previous work also assumed that the only source of anisotropic surface mass flow was an anisotropic diffusion constant $D$. Here we would like to also consider the possibility that the effective charge $q_{\text{eff}}$ of the adparticle may itself be anisotropic, in the sense that $q_{\text{eff}}$ is a tensor with non-equal principal components. Physically, this means that the angle between $\vec{F}$ and $\vec{E}$ may vary with $\theta$. We will provide physical motivation for this possibility later, and argue that the
electron wind force $\vec{F}_{\text{wind}}$ on Si(001) surfaces likely depends on the angle $\theta$ between $\vec{E}$ and the local surface dimer row direction. For the time being, we simply generalize Eq. (1) to:

$$\vec{v}_{\text{drift}} = \mu \vec{E},$$  \tag{2}$$

where the “surface mobility” tensor $\mu$ contains any anisotropy that may exist in either $D$ or $q_{\text{eff}}$. If one assumes a linear response between $\vec{v}_{\text{drift}}$ and $\vec{E}$, and time-reversal symmetry (i.e., no magnetic field), then the most general form of $\mu$ is a 2×2 symmetric tensor that should be diagonalized along the high-symmetry <110> axes of the crystal surface. Therefore, on type-1 and type-2 terraces $\mu$ takes the form

$$\mu_1 = \begin{pmatrix} \mu_\parallel & 0 \\ 0 & \mu_\perp \end{pmatrix} \quad \text{and} \quad \mu_2 = \begin{pmatrix} \mu_\perp & 0 \\ 0 & \mu_\parallel \end{pmatrix},$$  \tag{3}$$

respectively, where $\mu_\parallel$ and $\mu_\perp$ would be the observed surface mobilities (i.e., the ratio of $\vec{v}_{\text{drift}}/\vec{E}$) when $\vec{E}$ is aligned parallel and perpendicular to the local dimer rows, respectively. If $q_{\text{eff}}$ is a scalar, then $\mu_\parallel = q_{\text{eff}} D_\parallel / k_B T$ and $\mu_\perp = q_{\text{eff}} D_\perp / k_B T$, where $D_\parallel$ and $D_\perp$ are the diffusion constants for motion parallel and perpendicular to the dimer row direction, respectively. If $q_{\text{eff}}$ has a tensor nature, then $\mu_\parallel = (q_{\text{eff}})_\parallel D_\parallel / k_B T$ and $\mu_\perp = (q_{\text{eff}})_\perp D_\perp / k_B T$, where $(q_{\text{eff}})_\parallel$ and $(q_{\text{eff}})_\perp$ are the ratios of $\vec{F}/\vec{E}$ when $\vec{E}$ is aligned parallel and perpendicular to the local dimer rows, respectively.
Again following the approach of previous authors, we introduce $\bar{J}_1$ and $\bar{J}_2$, which are the adparticle drift-current densities on type-1 and type-2 terraces, respectively. These are given by

$$\bar{J}_1 = n_{ad} \mu_1 \vec{E} = n_{ad} E (\mu_\parallel \sin \theta \hat{x} + \mu_\perp \cos \theta \hat{y}), \quad (4)$$

$$\bar{J}_2 = n_{ad} \mu_2 \vec{E} = n_{ad} E (\mu_\perp \sin \theta \hat{x} + \mu_\parallel \cos \theta \hat{y}). \quad (5)$$

where $n_{ad}$ is the adparticle concentration. We assume here that $n_{ad}$ is roughly constant over the terraces, since the adparticle diffusion length at these temperatures is thought to be considerably larger than typical terrace widths (20-200 nm) existing prior to thermal annealing on the surfaces observed in this study. We expect this to be true based on recent work by Finnie et al. (Phys. Rev. Lett. 82 (1999) 2737), who estimated the diffusion length of Si adatoms on Si(111) at 1037°C to be $\sim 26$ μm. This was done by observing the nucleation of vacancy pits on large terraces under sublimation conditions. Related measurements by Tanaka et al. (Appl. Phys. Lett. 69 (1996) 1235) indicate that the diffusion length on Si(001) at temperatures at or above 1020°C is at least several μm.

[Using the results from the BCF theory of step flow in the limit of fast adparticle attachment/detachment at steps (see H. –C. Jeong and E. D. Williams, Surf. Sci. Rep. 34 (1999), p. 205), the difference between the maximum and minimum values of $n_{ad}$ on a 1 μm wide terrace assuming a diffusion length of 2 μm is found to be about 3% of $n_{ad}(\text{max})$.] Strictly speaking, Eqs. (4) and (5) are only valid in the limits of negligible evaporation and fast step kinetics [36], i.e. when adparticle transport is diffusion-limited. However, Métois et al. [58] have argued that this limit is in fact appropriate for
describing island drift on Si(001), which depends on anisotropic surface mass flow in the
same way as step coupling. Furthermore, as described below, Eqs. (4) and (5) turn out to
agree very well with the step coupling behavior we have observed on our dimpled
samples. We emphasize, however, that our observations do not rule out the possibility
that a non-negligible step attachment/detachment barrier may also exist on the Si(001)
surface. As for step bunching, the specific choice of step “boundary conditions” (e.g.
relative rates of terrace diffusion and step attachment/detachment) does not affect the
overall symmetry of the bunching patterns, which is the important feature of the
following analysis. We will discuss this point in more detail below.

Next, we consider the adparticle flux onto steps. We define \( F_1^{U} \) and \( F_1^{L} \) as the ad-
particle drift-current flux onto an \( S_1 \)-step from the upper- and lower- terrace, respectively,
and the corresponding quantities \( F_2^{U} \) and \( F_2^{L} \) for the upper- and lower-terrace flux onto
\( S_2 \)-steps. These are given by \( F_1^{U} = \vec{J}_1 \cdot (-\hat{n}) \), \( F_1^{L} = \vec{J}_2 \cdot \hat{n} \), \( F_2^{U} = \vec{J}_2 \cdot (-\hat{n}) \),
and \( F_2^{L} = \vec{J}_1 \cdot \hat{n} \). We then consider the net adparticle flux \( \Delta F_1 = F_1^{U} + F_1^{L} \) onto \( S_1 \)-
steps, and \( \Delta F_2 = F_2^{U} + F_2^{L} \) onto \( S_2 \)-steps. After a little algebra, these can be expressed as:

\[
\Delta F_1 = n_{ad} E (\mu_\parallel - \mu_\perp) \cos(2\theta - \phi), \tag{6}
\]

\[
\Delta F_2 = -n_{ad} E (\mu_\parallel - \mu_\perp) \cos(2\theta - \phi) = -\Delta F_1. \tag{7}
\]

For the special case of \( \theta = 0 \), \( \phi = 0 \), and scalar \( q_{\text{eff}} \), Eqs. (6) and (7) are essentially
equivalent to the expression derived by Stoyanov to describe the step coupling on Si(001)
surfaces [36] and by Métois et al. [58] to describe island drift on Si(001).
3.5.2 Step coupling

We would now like to compare these expressions to the experiments shown in Figs. 3.2, 3.4, and 3.5. We first consider how a direct current induces step coupling on Si(001), following the general ideas first proposed by Latyshev [45]. Let us assume for the moment that $\mu_\parallel - \mu_\perp > 0$. If $\cos(2\theta - \phi) > 0$, we then have $\Delta F_1 > 0$ and $\Delta F_2 < 0$. This will add atoms to $S_1$-steps, causing them to advance (increasing the size of the trailing type-1 terrace) while $S_2$-steps will retract (shrinking the type-2 terraces). Eventually, $S_1$ and $S_2$ steps will approach each other to form a coupled step, leaving the surrounding terraces predominantly type-1. When $\cos(2\theta - \phi) < 0$, the steps will couple in the opposite way, leaving the surrounding terraces predominantly type-2. On a dimpled sample with circular symmetry, $\phi$ can be varied from 0 to $2\pi$ simply by moving to different locations around the dimple center. After the steps couple, we therefore expect that type-1 terraces will be dominant on half of the dimple, while type-2 terraces will be dominant on the other half. The dividing line between the two regions is determined by the requirement that $\cos(2\theta - \phi) = 0$. This line passes through the dimple center, and is rotated from horizontal by an angle of $2\theta$. For the case of $\theta = 0$ ( $\vec{E}$ parallel to [110], as in Figs. 3.2, 3.4, and 3.6a), we therefore expect a horizontal dividing line, with type-1 terraces dominant on the top half of the dimple and type-2 terraces dominant on the bottom half. As discussed in Section 4, this configuration is in fact what we have observed when $\theta = 0$, and justifies our assumption that $\mu_\parallel - \mu_\perp > 0$. The observed configuration is also just what one would expect based on the original work by Latyshev, namely that when $\vec{E}$ is parallel to a $<110>$ direction, then the dominant terrace has dimer rows perpendicular to
\( \vec{E} \) for step-up current (on the top half of the dimple), and parallel to \( \vec{E} \) for step-down current (bottom half of the dimple).

The predicted step coupling behavior is more surprising when \( \vec{E} \) is not parallel to a \(<110>\) direction. For the case of \( \theta = \pi/4 \) (\( \vec{E} \) parallel to \([010]\)), we would expect a vertical dividing line separating the two regions of the dimple, with type-1 terraces dominant on the left side of the dimple (if \( \mu_\parallel - \mu_\perp > 0 \)), and type-2 terraces dominant on the right side. As discussed earlier, this particular configuration of type-1 and type-2 terraces is indeed what we observe experimentally on samples with \( \theta = \pi/4 \) (Figs. 3.5 and 3.6b).

### 3.5.3 Step bunching

Although the observed step coupling indicate that \( (\mu_\parallel - \mu_\perp) > 0 \), it is important to realize that the observed coupling behavior does not by itself determine the magnitude or even the sign of \( \mu_\parallel \) or \( \mu_\perp \) individually. As long as \( \mu_\parallel \) is more positive than \( \mu_\perp \), then we would get the same step coupling behavior whether \( \mu_\parallel \) and \( \mu_\perp \) were both positive, both negative, or had opposite sign. This means that step coupling cannot by itself be used to determine the magnitude or even the direction of the adparticle currents \( \vec{J}_1 \) and \( \vec{J}_2 \) on type-1 and type-2 terraces. We note here that the same is true of the island experiments of Métois et al. [58], which are believed to depend on anisotropic mass flow in the same way as step coupling.
To investigate the actual direction of $\vec{J}_1$ and $\vec{J}_2$ in more detail, we need to monitor physical behavior which depends more directly on the direction of $\vec{J}_1$ and $\vec{J}_2$ individually. We will do this by observing the large-scale step bunching patterns around our dimpled samples. The basic idea is the following: according to the leading theories of electromigration-induced step bunching [36-39;40], the step bunching behavior depends critically on whether the sense of the adparticle current is step-up or step-down. On a dimpled sample that has an adparticle current flowing in a particular (but unknown) direction, the sense of the adparticle current will cross-over from step-up to step-down at dimple locations where the step edges are oriented parallel to the adparticle current direction. Hence the presence (or absence) of transisitions in step bunching behavior at specific dimple locations should tell us something about the absolute direction of the adparticle current. We should note that the two leading step bunching theories differ from each other in many key aspects. In particular, their assumptions about the step boundary conditions (e.g. step permeability and the inclusion of an attachment/detachment barrier) differ, as do their specific predictions for whether a step-up or step-down adparticle current is necessary for bunching. However, both theories agree that under a particular set of sample conditions (e.g. temperature, step permeability), step bunching is expected for only one sense of the adparticle current. Hence, if either theory applies to Si(001) surfaces, we should see some sort of transition in step bunching behavior where the steps are locally parallel to the adparticle current, independent of our specific choice of step boundary conditions.
We will consider two specific models for the adparticle flow anisotropy, and compare each with the measured step bunching patterns for $\theta = 0$ and $\theta = \pi/4$. We emphasize that these models attempt to describe the adparticle flow (in particular, the direction of adparticle drift) and do not attempt to describe the bunching process itself.

3.5.3.1 Conventional view of electromigration on Si(001)

We start with model “A”, which is essentially the model considered previously in the literature [46]. This model assumes that $q_{\text{eff}}$ is a scalar, and assumes faster diffusion parallel to the dimer row direction ($D_\parallel > D_\perp$). Since the observed step coupling indicates that $\mu_\parallel - \mu_\perp > 0$, then model A requires that a scalar $q_{\text{eff}}$ be positive, and hence that both $\mu_\parallel$ and $\mu_\perp$ must be positive.

We first consider $\theta = 0$, i.e. the applied field is oriented along $[\bar{1}0\bar{1}]$. As explained above, the step coupling is such that the surface on the top (bottom) of the dimple consists almost exclusively of type-1 (type-2) terraces. We therefore expect that adparticle flow is dominated by $\vec{J}_1$ ($\vec{J}_2$) on the top (bottom) half of the dimple. When $\theta = 0$, Eqs. (4) and (5) indicate that both $\vec{J}_1$ and $\vec{J}_2$ should be parallel to the $+\hat{y}$ direction, which by definition is aligned along the $[\bar{1}0\bar{1}]$ crystal direction. Model A therefore implies a step-up adparticle flow on the top half of the dimple, and a larger-magnitude step-down flow on the bottom half. Since the anisotropy in the diffusion constant $D$ has not been quantified at the temperatures considered here, we will consider the two extreme limits, i.e. (i) nearly isotropic diffusion ($\mu_1 \geq \mu_\perp$) and (ii) highly anisotropic diffusion ($\mu_1 \gg \mu_\perp$). The predicted adparticle flow in these limits is shown in Figs. 3.6c and 3.6e.
We next consider the step bunching patterns that should form with this kind of surface mass flow. As mentioned earlier, two leading models for electromigration-induced step bunching both predict that bunching should only occur for one sense of the surface adparticle flow for a given annealing condition, but differ as to whether step-up or step-down flow is required for bunching. If step-down flow is required, then bunching should occur (within model A) only on the bottom half of the dimple, as illustrated by the dark curved bands in Figs. 3.6c and 3.6e. If step-up flow is required for bunching, then bunching would be expected only on the top half of the dimple (not shown). It is clear that neither scenario agrees with the observed step bunching patterns (Figs. 2, 4, and 3.6a) which show that bunching occurs on both sides of the dimple.

We next consider the case of \( \theta = \pi/4 \), for which the applied field is oriented 45° to the surface dimer rows. As mentioned previously, the observed step coupling in this case is such that the terraces on the left (right) half of the dimple are almost exclusively type-1 (type-2), so the adparticle flow should be dominated by \( \vec{J}_1 \) (\( \vec{J}_2 \)) on the left (right) half of the dimple. When \( \theta = \pi/4 \), Eqs. (4) and (5) give

\[
\vec{J}_1 = n_{ad} \mu_1 \vec{E} = n_{ad} E / \sqrt{2}(\mu \hat{x} + \mu \hat{y}) \quad \text{and} \quad \vec{J}_2 = n_{ad} \mu_2 \vec{E} = n_{ad} E / \sqrt{2}(\mu \hat{x} + \mu \hat{y}) .
\]

The limit of near isotropic diffusion (\( \mu \parallel \geq \mu \perp \)) is illustrated in Fig. 3.6d. In this case, both \( \vec{J}_1 \) and \( \vec{J}_2 \) should be almost parallel to \( \vec{E} \), so the adparticle flow would be step-down over most of the bottom half of the dimple, and step-up over most on the top half. One would then expect bunching on either the top half or bottom half of the dimple, with a roughly horizontal transition line between the two regions, as illustrated in Fig. 3.6d. This is clearly very different from the observed bunching behavior (Figs. 3.5 and 3.6b),
which has strong bunching to the sides of the dimple, little bunching near the top or bottom, and a *vertical* transition line between the two bunched regions. Hence model $A$ with $\mu_\parallel \geq \mu_\perp$ is in strong disagreement with the observed bunching behavior.

We also consider model $A$ in the limit of highly anisotropic diffusion, *i.e.* $D_\parallel \gg D_\perp$, which implies that $\mu_\parallel \gg \mu_\perp$. In this case, we expect that the surface adparticle flow would be nearly parallel to the local dimer row direction, as illustrated in Fig. 3.6f. If a step-down flux is required for bunching, we would expect the step bunching pattern shown in Fig. 3.6f, with the strongest bunching on the bottom of the dimple, no bunching on the top, and weaker bunching on the sides of the dimple. This does not agree with the observed bunching when $\theta = \pi/4$ (see Figs. 5 and 3.6b), which shows the bunching to be strongest on the sides, and weaker or no bunching on the top and bottom parts of the dimple. Furthermore, model $A$ predicts that the adparticle flow would change from step-up to step-down at $\phi = \pm \pi/4$, and hence we would expect a significant change in bunching behavior at this angle, as illustrated by the dashed line in Fig. 3.6f. However, the observed step bunching behavior is quite uniform as $\phi$ passes through $\pm \pi/4$, and only shows a significant change in character much closer to the vertical.

If the diffusion anisotropy happens to be anywhere between these two limits, we would still expect to see a significant difference in bunching on the top half and bottom half of the dimple, and expect to observe a transition line for step bunching to exist somewhere between $\phi = 0$ and $\pm \pi/4$. However, the observed bunching for $\theta = \pi/4$ is relatively similar on the top and bottom of the dimple, and shows no apparent change in bunching behavior for $\phi$ between 0 and $\pi/4$. We therefore conclude that model $A$ cannot
account for the observed step bunching, at least within the framework of the proposed step bunching models.

3.5.3.2 Alternative description

Given the failure of model A to account for the our observations of step bunching on Si(001), we postulate another possibility (model ‘B”), which assumes that the effective charge \( q_{\text{eff}} \) is a tensor, and is sufficiently anisotropic that \( \mu_\parallel \) and \( \mu_\perp \) have different polarity. This in turn requires a that \( \mu_\parallel > 0 \) and \( \mu_\perp < 0 \), since the observed step coupling requires that \( \mu_\parallel - \mu_\perp > 0 \). We first consider the expected bunching behavior from model B if \( \mu_\parallel \) and \( \mu_\perp \) have similar magnitude, in which case \( \mu_\parallel \equiv -\mu_\perp \). For the case \( \theta = 0 \), Eqs. (4) and (5) would imply that \( \vec{J}_1 \) and \( \vec{J}_2 \) point along \( \hat{y} \) and \( -\hat{y} \), respectively, and hence point in opposite directions. The resulting adparticle flow is illustrated in Fig. 3.6g. In this case, there would be a step-down adparticle flow on both halves of the dimple. If a step-down flow produces bunching, then the expected bunching would be on both the top and bottom of the dimple, with less bunching directly to the sides. This is similar to the observed bunching behavior for \( \theta = 0 \) (see Figs. 2, 4 and 3.6a).

For the case of \( \theta = \pi/4 \) (and still assuming \( \mu_\parallel \equiv -\mu_\perp \)), Eqs. (4) and (5) would imply that \( \vec{J}_1 \) and \( \vec{J}_2 \) point in nearly opposite directions, and furthermore are both aligned nearly perpendicular to \( \vec{E} \). This surprising flow pattern is illustrated in Fig. 3.6h, where we see that the adparticle flow would be step-down on both the right and the left halves of the dimple. Thus, we would expect bunching on both the right and left of the dimple, with less bunching directly to the top and bottom. Again, this is similar to the observed
bunching when $\theta = \pi/4$ (see Figs. 5 and 3.6b). Hence, model B predicts bunching behavior that is quite consistent with the observed behavior for both $\theta = 0$ and $\theta = \pi/4$.

We should also consider the possibility that $\mu_\parallel$ and $\mu_\perp$ have opposite polarity, but substantially different magnitudes. For the case of $\theta = 0$, and assuming $|\mu_\parallel| > |\mu_\perp|$, Eqs. (4) and (5) imply an adparticle flow pattern as illustrated in Fig. 7i. In this case, $\vec{J}_1$ and $\vec{J}_2$ would still point in opposite directions, but would have different magnitude. This should still produce bunching on both the top and bottom halves of the dimple (in agreement with experiment), but the bunching might not be identical on the two halves. Fig. 7j shows the expected flow pattern for the case of $\theta = \pi/4$ (still assuming $|\mu_\parallel| > |\mu_\perp|$). In this case, there is a slight “upward” component of the flow, so one might expect qualitatively different bunching on the top- and bottom-halves of the dimple, and a wedge-shaped transition zone on one side of the dimple, as indicated in Fig. 7j. Since the experimentally observed bunching at the top and bottom parts of the dimples are not exactly alike, model B would allow some difference in the magnitudes of $\mu_\parallel$ and $\mu_\perp$ while still maintaining good agreement with the observed step bunching behavior.

3.5.4 **Physical motivation for an anisotropic electromigration force**

Model B is very appealing because it predicts surface adparticle flow that would produce the observed step coupling and step bunching behavior, both for the case $\vec{E}$ along [101] ($\theta = 0$), as well as $\vec{E}$ along [010] ($\theta = \pi/4$). However, this model requires that the effective charge $q_{\text{eff}}$ of the adparticle have a highly anisotropic tensor nature. We
now wish to physically motivate this possibility. As discussed earlier, the net electromigration force $\vec{F}$ is generally thought $[59]$ to be the sum of a direct electrostatic force $\vec{F}_{\text{direct}} = q_{\text{direct}} \vec{E}$ and an electron-wind force $\vec{F}_{\text{wind}} = q_{\text{wind}} \vec{E}$. There are at least two reasons why $q_{\text{wind}}$ likely does have a tensor nature on the Si(001)-(2×1) surface. First, the drift velocity of electrons at the surface of Si(001) likely depends on the angle $\theta$ between $\vec{E}$ and the surface dimer rows. Deep in the Si bulk, the cubic symmetry of the (bulk) Si lattice requires an isotropic electron mobility. But this symmetry is broken on the Si(001)-(2×1) surface, which has biaxial (not square) in-plane symmetry. For example, the surface dimer rows might "channel" surface electron flow, causing the surface electron drift velocity (and hence the electron-wind force) to vary with the angle $\theta$.

A second possible reason for a tensor $q_{\text{wind}}$ has to do with the anisotropic shape of the diffusing surface adparticle itself. Recent studies $[80]$ indicate that the diffusing species on Si(001) are actually an ad-dimer, even up to the temperatures considered here, which furthermore has a preferred orientation $[60]$ with respect to the surface dimer rows. This preferred orientation is illustrated in Fig. 3.10. It therefore seems likely that the surface-electron/ad-dimer cross-section would be anisotropic, with corresponding anisotropy in the electron-wind force. One would expect the electron-wind force $\vec{F}_{\text{wind}}$ to be maximum when the dimer is "broadside" to the electron wind (Fig. 3.10a), be minimum when the dimer is pointing “into” the electron wind (Fig. 3.10b), and would have an intermediate magnitude and a sideways component of the force when the dimer is at an intermediate angle to the electron wind (Fig. 3.10c).
Any anisotropy resulting from the above two mechanisms would result in a tensor $q_{\text{wind}}$, whose principal components $(q_{\text{wind}})_{\parallel}$ and $(q_{\text{wind}})_{\perp}$ are different from each other. However, we would expect that both components would be negative, since surface electrons will drift in approximately the opposite direction to $\vec{E}$. How then could the total effective charge tensor $q_{\text{eff}}$ have principal components that have opposite polarity?

We offer the following plausibility argument. Recall that $q_{\text{eff}} = q_{\text{direct}} + q_{\text{wind}}$, where $q_{\text{direct}}$ is the direct electrostatic charge of the adparticle. $q_{\text{direct}}$ is likely a scalar quantity (since it represents an actual charge), whose polarity depends on details of the adparticle/surface charge transfer. Theoretical studies by several groups [61,62] of Si(111) and Ge(111) surfaces suggest that negative charge tends to flow from the adparticle to the surface, and we therefore expect $q_{\text{direct}}$ to be positive. A more direct calculation of $q_{\text{direct}}$ on Si(111) [59] indicates that $q_{\text{direct}}$ on this surface is in fact positive. The principal components of $q_{\text{eff}}$ are $(q_{\text{eff}})_{\parallel} = q_{\text{direct}} + (q_{\text{wind}})_{\parallel}$ and $(q_{\text{eff}})_{\perp} = q_{\text{direct}} + (q_{\text{wind}})_{\perp}$. If $q_{\text{direct}}$ is positive on Si(001) with a similar magnitude to the (negative) values of $(q_{\text{wind}})_{\parallel}$ and $(q_{\text{wind}})_{\perp}$, then the net effective charge $q_{\text{eff}}$ would have principal components that were closer to zero, and could even have opposite polarity. This is also illustrated in Fig. 3.10, which shows the resulting forces acting on an ad-dimer when $\vec{E}$ is perpendicular (Fig. 3.10a), parallel (Fig. 3.10b), or at a 45° angle (Fig. 3.10c) to the surface dimer rows. Fig. 3.10 is drawn assuming $|(q_{\text{wind}})_{\perp}| > |q_{\text{direct}}| > |(q_{\text{wind}})_{\parallel}|$.

This scenario is somewhat analogous to a popular model for the effective charge on Si(111) surfaces [59], which argues that a positive $q_{\text{direct}}$ largely cancels a negative $q_{\text{wind}}$, permitting small (temperature-dependent) changes in the magnitudes of $q_{\text{direct}}$ and $q_{\text{wind}}$ to
cause reversal in the polarity of \( q_{\text{eff}} \) with increasing temperature [59]. Our proposal for Si(001) is similar in that a positive \( q_{\text{direct}} \) mostly cancels a \( q_{\text{wind}} \) tensor with negative magnitude, leaving an effective charge tensor whose principal components have different polarity.

3.5.5 Possible Ehrlich-Schwoebel barrier effects

The analysis above assumes that step bunching arises from electromigration of surface adparticles. However, step bunching is also predicted to occur if there exists an ESB for adatom attachment/detachment at steps [54-57]. As discussed above, we do not believe a simple ESB can account for our observations. However, it is interesting to note that Figs. 3.6a and 3.6b show that the symmetry of the step bunched areas "follows" the symmetry of the step coupling as the direction of the applied current is changed from the [\( \bar{1} 10 \)] to the [010] crystal direction. In Fig. 3.6a, the (horizontal) transition line between the bunched regions is also where the majority domain switches from \((2\times1)\) to \((1\times2)\), and in Fig. 3.6b, the vertical transition line between the bunched regions is also where the coupling switches. This leads us to propose another possible mechanism that could produce the bunching patterns shown in Figs. 3.2, 3.4, and 3.5, namely that the observed bunching could be due to a coupling-induced ESB-effect. In other words, the “role” of the applied direct current is to induce step coupling. From then on, step bunching proceeds via the ESB-mechanism. At present, we have no reason for believing that such an ESB mechanism actually exists, but if it did, it would produce bunch patterns similar to those we have observed.
3.6 Conclusions

We have investigated surface mass transport on Si(001) surfaces heated with direct current by observing step coupling and step bunching behavior on these surfaces. On surfaces heated with direct current applied along the [\bar{1}10] crystal direction, step bunching is observed for both step-up and step-down current simultaneously, similar to behavior observed previously by other groups [41-44]. This is unlike Si(111) surfaces, where our observations, as well as those of other groups [30], show that bunching occurs for only one sense (i.e. step-up or step-down) of the applied current. Surprisingly, when the heating current is applied along the [010] crystal direction, step bunching occurs predominantly in areas of the sample where the applied current is directed mostly parallel to the local step direction. Such behavior has not been previously reported. Hence, the top-bottom contrast in the bunching patterns observed on our spherically dimpled surfaces heated with the applied current along the [\bar{1}10] crystal direction gives way to a left-right contrast when the external field is applied along the [010] crystal direction. We have shown that these observations are not consistent with the assumptions of i) anisotropic diffusion and ii) an isotropic adparticle effective charge $q_{\text{eff}}$, which have until now comprised the conventional view of Si(001) DC-induced surface mass transport. Rather, our observations suggest that the surface mass flow can be either parallel, anti-parallel, or sideways to the applied electric field $\vec{E}$ (depending on the angle between $\vec{E}$ and the surface dimer rows), and we propose that this could result from an anisotropic effective charge.
Fig 3.1. Dimpled Si(111) surface heated with direct current to 1200°C for 30 min. The applied field is directed upward in the image. (a) Optical large-scale micrograph showing the area near the bottom of the dimple, which is marked “X”. (b) 30 µm derivative mode (DM) AFM close-up view of the region above the center of the dimple, where the current is applied in a step-up direction. Step bunches (wide, dark bands) are separated by terraces covered with sparse arrays of crossing steps (thinner, dark lines). (c) 15 µm DM-AFM close-up view of the region below the center of the dimple, where the current is applied in a step-down direction. Here, a uniform step train is observed.
Fig 3.2. Dimpled Si(001) surface heated to 990°C for 18 hours with the current applied along the crystal direction. (a) Optical large-scale micrograph showing the region near the bottom of the dimple. Step bunches are observed on both sides of the dimple. In areas where the current is applied in a step-up direction (upper half of the figure), step bunched areas coexist with step wandering patterns, which appear as straight “grooves” aligned with the crystal direction. (b) 60 µm and (c) 50 µm DM-AFM close-up views of the dotted regions in (a), showing step bunches separated by nearly step-free terraces. Both AFM scans should be viewed as if illuminated from the left.
Fig 3.3. (a) 40°60 µm² AFM image of step wandering patterns observed on a Si(001) surface heated to 1040°C for 32 hours with the current applied along the crystal direction. (b) Surface height profile measured along the dotted line in (a).
Fig 3.4. Dimpled Si(001) surface heated to 1040°C for 18 hrs with the current applied along the crystal direction. (a) Optical large-scale micrograph showing the bottom of the dimple, revealing step bunching on both sides of the dimple, as well as step bending patterns on the side of the dimple. (b-c) 50 µm DM-AFM close-up views of the dotted regions in (a). Both AFM images should be viewed as if illuminated from the left.
Fig 3.5. Dimpled Si(001) surface heated to 1040°C for 18 hours with the direct current applied along the [010] crystal direction. (a) Optical large-scale micrograph showing the region near the bottom of the dimple. Step bunching is observed predominantly on the sides of the dimple. (b) 15 µm DM-AFM close-up scan (view as if illuminated from the left) of a region in the vicinity of the area indicated by the heavy arrow in (a). (c) 30 µm AFM close-up view (view as if illuminated from the top) of the dotted region in (a). The parallel lines superimposed on the AFM scans in (b) and (c) indicate the dimer row direction on the majority terrace.
Fig 3.6. (previous page) (a-b) The observed symmetry of step bunching and coupling on Si(001) surfaces. The heavy, arced bands represent step bunches, whereas the thin lines show the direction of the dimer rows on the majority terrace after the steps have coupled. (a) For current applied along the crystal direction, bunching is strongest at the top and bottom of the dimple. (b) For current applied along the [010] direction, bunching is strongest to the sides of the dimple. (c-j) Predicted direction of adparticle flow on the majority terrace and the resulting step bunching pattern for the two models ("A" and "B") discussed in the text. The heavy dashed lines mark the positions at which the adparticle flow is parallel to the local step-direction, where a significant change in the bunching is expected. The thinner, dotted lines separate regions of the sample where the majority terrace is either type-1 or type-2. The dotted line is not shown if it coincides with the dashed line.
Fig 3.7. Composite of three 60 µm AFM images near the center of a dimpled Si(001) sample heated to 1040°C for 4.5 hrs, with current directed downward. Step bunches are seen near the top and bottom of the composite image. Parallel step bands due to a step-bending instability are observed off to the sides of the dimple, where the current is roughly parallel to the steps on the pristine surface.
Fig 3.8. (a) The middle image from Fig. 3.7. (b-c) 20 µm (b) and 30 µm (c) AFM close-up views of the boxed areas in Fig. (a). The average miscut in Fig. (b) is 0.08° to the left, i.e. toward the bottom of the dimple. (d) Schematic illustration of the wavy step patterns expected from the step-bending instability. (d) is based on Fig. 2 from Ref. [35].
Fig 3.9. Definition of the various angles and crystal directions used in the text.
(a) Schematic top view of a spherical dimple. The concentric, circular rings represent single-height surface steps. \( \phi \) is the angle between the applied field and the local step normal. (b) Close-up view of the boxed area in (a), showing three adjacent terraces, with the step-down direction toward the lower right part of the figure. The thin, parallel lines represent dimer rows, whose direction rotates \( 90^\circ \) as a step (heavy line) is crossed. Dimer rows on type-1 and type-2 terraces (see text) run along the \([110]\) and \([\bar{1}10]\) crystal directions, respectively. \( \theta \) is the angle between the applied field and the \( [010] \) direction. Hence, \( \theta = 0 \) \((\pi/4)\) for current applied along the \( [010] \) crystal direction. The terrace above “\( S_1 \)”- and “\( S_2 \)”-steps are type-1 and type-2 terraces, respectively (see text).
Fig 3.10. An ad-dimer and proposed surface electromigration forces when the applied electric field is (a) parallel, (b) perpendicular, or (c) at 45° to the surface dimer rows.
CHAPTER 4

STABILITY OF Si(001) TERRACES AGAINST SUBLIMATION PIT FORMATION

4.1 Introduction

It can be argued that the goal of surface science is not simply to understand the atomic processes governing the evolution of crystal surfaces, but also to apply that knowledge in order to manufacture surface morphologies of one’s choice. In this Chapter, I will demonstrate a method whereby we have done precisely that. In particular, I will outline a practical method for preparing ultra-large (tens of μm) step-free terraces on Si(001). Such large terraces are extremely useful for detailed studies of growth and other surface processes without the complication of existing surface steps [63,79], and for future device applications that require large, step-free areas [64].

Our method is an extension of the method by Tanaka et al. [15] and Homma et al. [16], who exploited an atomic-scale understanding of surface phenomena to prepare arrays of large (> 5 μm) step-free terraces on Si(001) and Si(111) surfaces, respectively. The method of Tanaka et al. and Homma et al. first uses lithography to define “craters”
(depressions) on a Si wafer several µm across. Upon annealing at sublimation temperatures, closed steps near the bottom of a crater move toward the crater edges, leaving behind a large, step-free terrace. The maximum size of a terrace is limited by the nucleation of a new closed step in the form of a monolayer (ML) deep pit (or a “macrovacancy”) due to build up of terrace vacancies [65]. Pit nucleation generally occurs near the center of a terrace, since steps at the terrace edge serve as a source of mobile terrace adparticles [66] (probably adatoms for Si(111) and ad-dimers for Si(001) [63]) which fill terrace vacancies, and/or a sink for mobile terrace vacancies. The maximum terrace size (before pit nucleation) has been observed to increase at reduced annealing temperature [15] due to a longer adparticle diffusion length $\lambda = \sqrt{D\tau}$, where $D$ is the adparticle diffusion constant and $\tau$ is the adparticle desorption lifetime. We note that $\tau$ increases while $D$ decreases at lower temperature, but the increase in $\tau$ is stronger due to its larger activation energy. A longer $\lambda$ reduces the lateral variation in the adparticle and vacancy concentrations away from the steps at the terrace edge [65,66], and hence increases the maximum terrace size before pit nucleation occurs. However, reduced sublimation also reduces the velocity of step retraction, imposing a practical limit of how large a crater can be flattened in a reasonable time. It would clearly be desirable to somehow increase terrace stability without reducing the step velocity, in order to produce larger step-free surfaces on practical time scales.

Here we demonstrate that such enhanced terrace stability can indeed be achieved by raising the sample temperature by an amount $\Delta T$ while adding a small Si flux $R$ to maintain a constant net sublimation rate. In essence, this results in faster diffusion (larger
while maintaining a constant effective adparticle lifetime $\tau_{eff}$, where $\tau_{eff}^{-1} \equiv (\tau^{-1} - R/c_{eq})$ and $c_{eq}$ is the equilibrium ad-particle concentration on the terrace. This produces a larger effective diffusion length $\lambda_{eff} = \sqrt{D\tau_{eff}}$, resulting in a more stable terrace with the same step retraction velocity. We have verified this enhanced terrace stability using real-time measurements of high-temperature terrace flattening using low energy electron microscopy (LEEM), and through kinetic modeling of step motion. Our modeling indicates that this enhanced terrace stability should be greatly increased by using a larger temperature increase with a correspondingly larger Si flux. Furthermore, our measurements and modeling allow us to estimate lower limits on the adparticle concentration $c_{min}$ at which pits start to nucleate, and the related ad-article diffusion length $\lambda$. Both are important parameters for the understanding of high-temperature growth and annealing processes on Si surfaces.

4.2 Experiment

The samples used in this study were Si(001) wafers patterned with 50 µm – square craters, and were provided by NTT, Japan. Preliminary studies were done using similarly patterned samples provided by J. Blakely and C. Umbach at Cornell University. The surface roughness on the crater floor (due to the crater etching process) was removed by heating the sample to 1030-1050°C for many hours. The sample was then annealed in the range 1003-1043°C, where steady-state nucleation and expansion of concentric pits was observed (see Fig. 1). Sample temperature was measured using an infrared pyrometer with an estimated run-to-run uncertainty of ± 2°C, and an absolute uncertainty of ± 30°C.
The evolution of the surface (for Si flux $R = 0$ and $R \approx 0.007$ ML/s) was monitored in real time using LEEM. Diffraction contrast from the $(\frac{1}{2}, 0)$ diffracted beam from the Si(001)-(2×1) reconstruction produces the observed dark-bright contrast between adjacent terraces separated by a ML-high step [17].

### 4.3 Results

Fig. 4.1(a) shows a LEEM image of a Si(001) surface heated to 1015°C without flux, while Fig. 4.1(b) shows the same area with the additional Si flux during annealing at the same temperature. These images were recorded immediately after the nucleation of a new pit, which appear as the bright spots labeled ‘NP’ in the images. The central and next-larger terrace boundaries are labeled ‘S1’ and ‘S2’, respectively. Note that these labels do not have the same meaning as the labels ‘S1’ and ‘S2’ in Chapter 3. We denote $r_1$ and $r_2$ as the mean radii of $S1$ and $S2$, respectively, and $r_{1,max}$ as the radius of the central terrace at the instant a new pit forms. Adding a Si flux significantly increases the maximum size of the central terrace prior to pit nucleation, and reduces the density of concentric step-loops within the 50 µm depression.

Fig. 4.2(a) shows how the maximum terrace diameter $d_{1,max} = 2r_{1,max}$ depends on annealing temperature $T$, both with (open circles) and without (filled circles) the Si flux. The error bars are based on observations of multiple nucleation events at each temperature. The curves in the figure are the results of the model calculations described later. Adding a Si flux increases $d_{1,max}$, and this increase becomes larger at lower temperature. It is important to also monitor the speed $v_1$ of step $S1$ at the instant a new pit
forms. As seen in Fig. 4.2(b), $v_1$ increases at higher temperatures (due to enhanced sublimation) and is reduced by adding a Si flux during annealing.

Fig. 4.3(a) uses the same data as Fig. 4.2, but plots $d_{1,max}$ versus $v_1$ (with temperature an implicit parameter). The data points for annealing with flux (open circles) are shifted upwards with respect to the case of no added flux. This upward shift between the two data sets is significantly larger than the error bars shown in Fig. 4.2, and also agrees with the modeling discussed below. This means that the maximum terrace size can be increased (for the same step retraction speed) by raising the sample temperature and adding a small Si flux. From Fig. 4.3(a) we find that $d_{1,max}$ increases by ~2 µm at a pit expansion speed $v_1$ near 70 nm/s.

### 4.4 Model

We next model these LEEM observations within the framework of the Burton-Cabrera-Frank (BCF) theory of crystal surfaces [66], modified to include a finite step-terrace adparticle exchange rate [67]. Adparticle attachment/detachment from steps is characterized by a rate parameter $\kappa = \kappa_0 \exp(-\beta E_F)$, adparticle terrace diffusion by $D = D_0 \exp(-\beta E_D)$, the adparticle lifetime (before desorption) by $\tau = \tau_0 \exp(\beta E_\tau)$, and the adparticle formation energy (due to step detachment) by $E_F$, where $\beta \equiv 1/k_B T$ and $k_B$ is the Boltzmann constant. Under conditions of net sublimation, the steady-state adparticle concentration $c(r)$ on a terrace is given by $D \nabla^2 c(r) - c(r)/\tau + R = 0$, subject to the boundary condition $|\nabla c(r)| = \kappa [c_{eq} - c(r)]$ at the step edges [81]. Here, $c_{eq}$ is the equilibrium adparticle concentration (i.e., the concentration at which there would be no
movement of a straight step) and is given by  

\[ c_{eq} = a^2 \exp(-\beta E_F) \]  

[63], where \( a^2 = 0.29 \) nm² is the area of the diffusing adparticle, assumed here to be a surface dimer [63]. We note that for the large-radius steps considered here the step curvature makes a negligible contribution to \( c_{eq} \) [81]. To keep the model simple, we assume circular symmetry and (1) the same \( \kappa \) for attachment/detachment at ascending and descending sides of a step (i.e., no Ehrlich-Schwoebel barrier [68]), (2) that adparticles cannot cross a step without first attaching to it, and (3) isotropic \( D \) and \( \kappa \). With regard to this last assumption, we note that recent LEEM measurements [63,79] suggest that \( D \) becomes relatively isotropic on Si(001) at elevated temperatures (\( > 670^\circ C \)), and detailed modeling of surface processes at elevated temperatures appears to work well by assuming isotropic \( D \) and \( \kappa \) [79].

With these assumptions, the adparticle concentration \( c_1(r) \) on the innermost terrace is

\[
c_1(r) = R\tau + \left( \frac{c_{eq} - R\tau}{D\kappa} \right) \frac{I_0\left(\frac{r}{\lambda}\right)}{I_1\left(\frac{r_1}{\lambda}\right)} \left( I_0\left(\frac{r}{\lambda}\right) + I_1\left(\frac{r_1}{\lambda}\right) \right), \quad r < r_1
\]

(1)

where \( I_n \) is the modified Bessel function of \( n^{th} \) order. A somewhat more complicated solution \( c_2(r) \) can be found for the second terrace (for \( r_1 < r < r_2 \)), but for brevity is not shown here. The retraction speed of the innermost step \( S1 \) is given by

\[
v_1 = a^2 D \left[ \frac{dc_1(r)}{dr} \bigg|_{r_{max}} - \frac{dc_2(r)}{dr} \bigg|_{r_{max}} \right]
\]

(2)

As the innermost step loop expands, the adparticle concentration \( c_1(r=0) \) at the center of the terrace decreases, allowing the vacancy concentration to increase until a
new pit nucleates [65]. We assume this occurs when the ratio $c_1(r=0)/c_{eq}$ falls below a critical fraction $c_{min}/c_{eq}$.

Table 1 lists the parameter values in our model. Table 1(a) lists the values taken from the literature, and Table 1(b) lists several optimized sets of the adjustable parameters. The value $E_t \approx 4.0$ eV was determined assuming the sublimation rate $R_{sub} \approx c_{eq}/\tau \propto \exp[-(E_t + E_F)]$ [65] and using the reported activation energy of 4.3 eV for Si sublimation [69] and the value $E_F = 0.35$ eV [63]. $E_K$ and $\kappa_o$ were determined from an Arrhenius fit to reported values for the step mobility $\Gamma = \kappa \times c_{eq} \times a^4$ [81]. Since the reported values for $E_D$ differ greatly (~1 eV [70] to ~2 eV [63]), $E_D$ is an adjustable parameter in our model, but should have a value in the range 1 - 2 eV. The remaining adjustable parameters $D_o$, $\tau_o$, $R$, and $c_{min}/c_{eq}$ must have “reasonable” values such that (1) $R$ should be close to the value ~0.007 ML/s that we estimated from lower-temperature deposition measurements, (2) the sublimation rate $R_{sub} \approx c_{eq}/\tau$ should be close to the rate expected from Si vapor pressure data [ref], and (3) the atomic attempt rates $1/\tau_o$ and $4D_o/a^2$ [71] should be no larger than ~ $10^{14}$ - $10^{15}$ s$^{-1}$.

For a given set of parameter values, we calculate $d_{1,max} = 2r_{1,max}$ by finding the value of $r_1$ in Eq. (1) that yields $c_1(0) = c_{min}$. We then calculate the corresponding step velocity $v_1$ using Eq. (2). In our fitting procedure, we choose a trial value for $c_{min}/c_{eq}$, then adjust $E_D$, $D_o$, $\tau_o$, and $R$ to fit the data points both for $R = 0$ and for $R > 0$. The temperature dependence of the $R = 0$ data in Fig. 4.2(a) effectively determines $E_D$, with a value $E_D \approx 1.5$ eV giving the best fit. Details of the calculation are given in Appendix B. We find that a wide range of values for $c_{min}/c_{eq}$ (with appropriately adjusted values of $D_o$ and $\tau_o$)
can produce good fits to the \( R = 0 \) data. However, we are required to use \( \frac{c_{\text{min}}}{c_{\text{eq}}} > \sim 0.9 \) in order to get reasonable fits to both the \( R = 0 \) and \( R > 0 \) data. An example of a “poor” fit for \( \frac{c_{\text{min}}}{c_{\text{eq}}} = 0.8 \) is shown by the dashed line in Fig. 4.2(b), with corresponding parameter values listed in Table 1(b). In contrast, reasonably good fits to the data can be obtained for any value of \( \frac{c_{\text{min}}}{c_{\text{eq}}} \) between \( \sim 0.9 \) and 1. Table 1(b) shows the best parameter values for the case of \( \frac{c_{\text{min}}}{c_{\text{eq}}} = 0.9, 0.99, \) and 0.997. All three parameter sets give nearly the same fit, shown as the solid curves in Fig. 4.2 and Fig. 4.3(a). We note that the parameters \( \tau_0 \) and \( R \) are “reasonable” (as discussed above) and nearly constant for all three values of \( \frac{c_{\text{min}}}{c_{\text{eq}}} \), but that the diffusion attempt rate \( 4D_0/a^2 \) starts to become unreasonably high \( ( > 2 \times 10^{15} \text{ s}^{-1} ) \) for \( \frac{c_{\text{min}}}{c_{\text{eq}}} > 0.99 \). We also note that the model sublimation rate \( R_{\text{sub}} = \frac{c_{\text{eq}}}{\tau} \approx 0.6 \text{ ML/min at } 1000^\circ \text{C} \) is in rough agreement with the value \( \sim 1 \text{ ML/min} \) determined from published Si vapor pressure data [72].

It is important to emphasize that all these parameter sets reproduce quite well the observed “upward shift” of the data points in Fig. 4.3(a) for the case \( R > 0 \) (with Si flux), as compared to the case of no added flux. This indicates that enhanced terrace stability is a robust consequence of our simple model, and not dependent on the choice of particular parameter values. Furthermore, from the parameter values listed in Table 1(b) corresponding to the allowed range of \( \sim 0.9 < \frac{c_{\text{min}}}{c_{\text{eq}}} < 0.99 \), we estimate that \( \lambda \) is in the range of 10 to 30 \( \mu \text{m} \) at 1000\(^\circ\)C.

We note here that \( \frac{c_{\text{min}}}{c_{\text{eq}}} \) may in fact be temperature-dependent. In particular, a smaller step stiffness at higher temperature [25] would enhance pit nucleation for a given value of the adparticle concentration [65]. We have done tests where we assume that \( (1 – \)
\( \frac{c_{\text{min}}}{c_{\text{eq}}} \propto \exp(E_{\text{nucl}}/k_B T) \). This version of the model gives essentially identical fits as for the case when \( \frac{c_{\text{min}}}{c_{\text{eq}}} \) is constant, provided that the diffusion activation energy \( E_D \) is increased by an amount \( E_{\text{nucl}} \) (with \( D_0 \) adjusted accordingly). Hence, our original model (with constant \( \frac{c_{\text{min}}}{c_{\text{eq}}} \)) implicitly “absorbs” any temperature-dependence of \( \frac{c_{\text{min}}}{c_{\text{eq}}} \) by adjusting the best-fit values of \( E_D \) and \( D_0 \). We note that our model reproduces the observed temperature dependence of \( d_{1,\text{max}} \) extremely well (see Fig. 2(a)), indicating that any temperature dependence of \( \frac{c_{\text{min}}}{c_{\text{eq}}} \) is implicitly included.

If this model and parameter values are approximately correct, then the model can be used to predict how large this enhanced terrace stability should be with larger Si flux \( R \) and corresponding larger temperature increase. Fig. 4.3(b) shows the predicted maximum terrace diameter \( d_{1,\text{max}} \) vs. step speed \( v_1 \) for \( R = 0 \) and several values of flux up to \( R = 0.10 \) ML/s. The model suggests that the increase in the maximum terrace size could be more than doubled for \( v_1 = 80 \) nm/s using a modest deposition flux of 0.06 ML/s, with an even larger increase at lower \( v_1 \).

Finally, we return to our suggestion that the enhanced terrace stability can be mostly understood by invoking an effective adparticle lifetime \( \tau_{\text{eff}} \). With regard to the model, we note that the net desorption term \( (c_1(r)/\tau - R) \) in the diffusion equation is approximately equal to an effective sublimation rate \( c_1(r)/\tau_{\text{eff}} \) (where \( 1/\tau_{\text{eff}} \equiv 1/\tau - R/c_{\text{eq}} \)) provided that \( c_1(r) \) does not deviate much from \( c_{\text{eq}} \) across the terrace. This is consistent with our conclusion that \( \frac{c_{\text{min}}}{c_{\text{eq}}} > 0.9 \). We have verified that solving the diffusion equation with an effective sublimation term indeed gives a solution for \( c_1(r) \) that is almost identical to the solution shown as Eq. (1).
4.5 Summary

We have found that depositing Si while sublimating at elevated temperatures enhances terrace stability, leading to larger step-free Si(001) terraces at a given step retraction speed. We have shown that a simple model based on a modified BCF theory captures the essential physics of the enhancement, namely that increasing temperature results in an increased ‘effective’ diffusion length $\lambda_{\text{eff}} = \sqrt{D\tau_{\text{eff}}}$ . Furthermore, the model yields an estimate of the adparticle diffusion length in the range of 10 - 30 µm, and an estimate for the value $c_{\text{min}}/c_{\text{eq}}$ between .9 and 1. The model further suggests that greatly enhanced terrace stability (increased terrace size by factor of 2 or 3) at practical step speeds (~100 nm/s) can be realized by using larger Si fluxes of about 0.1 ML/s.
Fig 4.1. LEEM images of a Si(001) surface heated to 1015°C (a) without and (b) with added Si flux. © Schematic representation of the LEEM images in (a) and (b)
Fig 4.2. (a) Plot of maximum diameter $d_{1,max}$ of step $S1$ versus annealing temperature $T$, with added Si flux (open circles) and without (filled circles). (b) Speed $v_1$ of step $S1$ as new pit nucleates plotted against $T$. The solid and dotted lines show model calculations for $c_{\text{min}}/c_{eq} > 0.9$ and for $c_{\text{min}}/c_{eq} = 0.8$, respectively.
Fig 4.3. (a) Maximum pit size $d_{1,max}$ versus step speed $v_1$, with added Si flux (open circles) and without (filled circles). Lines are model calculations. Added flux shifts data points upward, indicating enhanced terrace stability at a given step speed $v_1$. (b) Calculated results for deposition rates $R = 0, 0.02, 0.04, 0.06, 0.08,$ and $0.10$ ML/s.
Table 1. Model parameter values for calculated curves in Figs. 2 and 3(a). (a) Values extracted from the literature and (b) adjustable parameters.

(a)

<table>
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<tr>
<th>$\kappa_0$</th>
<th>$E_\kappa$</th>
<th>$E_\tau$</th>
<th>$E_F$</th>
</tr>
</thead>
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<tr>
<td>$1.9 \times 10^{10}$ nm/s [81]</td>
<td>1.0 eV [81]</td>
<td>4.0 eV [63,69]</td>
<td>0.35 eV [63]</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
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<th>$E_D$ (eV)</th>
<th>$c_{min}/c_{eq}$</th>
<th>$D_o$ (nm$^2$/s)</th>
<th>$1/\tau_o$ (s$^{-1}$)</th>
<th>$R$ (ML/s)</th>
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<td>$6.5 \times 10^{12}$</td>
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</tr>
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<td>1.45</td>
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<td>$1.4 \times 10^{13}$</td>
<td>$1.8 \times 10^{15}$</td>
<td>0.007</td>
</tr>
<tr>
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<td>$1.5 \times 10^{14}$</td>
<td>$1.7 \times 10^{15}$</td>
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</tr>
<tr>
<td>1.6</td>
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<td>$2.2 \times 10^{15}$</td>
<td>$1.7 \times 10^{15}$</td>
<td>0.008</td>
</tr>
</tbody>
</table>
CHAPTER 5

Si(001) ADATOM DIFFUSION ANISOTROPY

5.1 Introduction

During thermal processing and epitaxial growth of semiconductor surfaces, a critical surface process is that of diffusion of adsorbed surface atoms. At relatively low temperatures (<128°C), real-time STM measurements [73,74] of the surface diffusing species (believed to be an addimer [75,76,63]) indicate that adatom diffusion on Si(001) is highly anisotropic, with diffusion being at least 1000 times faster along than across the surface dimer rows. At higher temperatures, the increased thermal adatom motion makes it impractical to track the motion of individual atoms using STM, and hence to verify directly whether the diffusion anisotropy persists to higher temperatures. Instead, information about the diffusion anisotropy at elevated temperatures can be found from the width of so-called “denuded zones” that form near pre-existing (vicinal) step-edges following Si(001) homoepitaxial growth of two-dimensional islands [77,78]. Several such growth studies [77] indicate that adatom diffusion remains anisotropic with increasing temperature, at least up to 330°C. However, recent observations by Bartelt et
al. [79] and Tromp et al. [76] of denuded zones at much higher temperatures (670-1000°C) seem to suggest that adatom diffusion at these higher temperatures is in fact largely isotropic. This is surprising, since this would seem to suggest that a fundamental surface change takes place between 330°C and 670°C, such as for example a change in the surface reconstruction or the emergence of isotropic diffusion pathways at elevated temperatures [63]. However, no independent evidence exists for such fundamental surface changes in this intermediate temperature range.

Here we report real-time low-energy electron microscopy (LEEM) observations and microscopic modeling of denuded zones during Si(001) homoepitaxial growth at temperatures in the 530-700°C range. Contrary to previous reports, we show that diffusion remains anisotropic at temperatures up to at least 800°C, the highest temperature available in our experiment. We resolve the apparent discrepancy between our observations and those of previous authors by demonstrating that the denuded zone width following 2-D island growth is highly sensitive to precisely how 2-D island formation is promoted. Furthermore, by comparing our observations with a simple model for the adatom concentration on the surface during the initial stages of Si deposition, we estimate that Si(001) adatom diffusion at 630°C is at least ~10 times faster along dimer rows than across them.

5.2 Experiment

Two-dimensional Si islands were grown by depositing Si from a thermal evaporation source onto large, step-free Si(001) terraces [see Chapter 4 for a discussion on how such step-free terraces are prepared]. The initial flattening of the patterned craters and the
subsequent 2-D island growth during Si deposition was monitored in real-time using LEEM. Sample temperature was measured using an infrared pyrometer with an estimated run-to-run uncertainty of ± 2°C, and an absolute uncertainty of ± 30°C.

5.3 Results

Figs. 5.1(a) - 5.1(d) shows LEEM images of a ~ 5×6 µm², initially step-free Si(001) terrace after depositing Si at a rate of 0.2 ML/min at several different temperatures ranging from 530°C to 700°C. At each deposition temperature, we observe a high density of 2-D islands, with the density of islands increasing with decreasing temperature. This is to be expected, since for a given Si deposition rate, and hence for a given adatom “supersaturation”, the lower adatom diffusion rates at lower temperatures translates to an increased likelihood that a deposited atom will join with other diffusing adatoms to form a new island, rather than joining a previously formed island. The islands all appear in the LEEM images nearly simultaneously across the terrace a few seconds after turning on the Si flux, as illustrated in Fig. 5.2. Figs. 5.2(a) and 5.2(b) show the same terrace as in Fig. 5.1 after depositing Si at a rate of .2 ML/min for 4 and 16 sec, respectively. We see that the island size distribution and density in Fig. 5.2(a) is quite uniform across the surface, indicating that islands have nucleated simultaneously across the surface. During subsequent Si deposition (Fig. 5.2(b)), few or no additional islands nucleate, and all incoming Si atoms attach either to existing islands or to the step-edges at the terrace boundary. Near the boundary of the large terrace, there is a “denuded” zone in which no islands form. This denuded zone forms because atoms that are deposited near the terrace
boundary can migrate to the terrace boundary before combining with other adatoms to form islands. The width of the denuded zone is generally assumed to increase with faster adatom diffusion [77]. Hence, by comparing the denuded zone widths $w_{||}$ and $w_{\perp}$ (see Fig. 5.1) that arise due to adatom diffusion parallel and perpendicular to the terrace dimer rows, respectively, one can determine (at least qualitatively) the diffusion anisotropy. In Fig. 5.1, the denuded zone widths are quite anisotropic (with $w_{||} > w_{\perp}$), which suggests that diffusion is in fact anisotropic at these temperatures, with faster diffusion along the dimer rows. From similar experiments using larger step-free areas than that shown in Fig. 5.1, we have determined that diffusion remains anisotropic up to at least 800°C, the highest temperature available in our growth experiments. Note that the maximum temperatures at which we can observe island formation is limited by (i) the Si deposition rate, which is limited in these experiments to about .01 ML/s using our thermal evaporation source, and (ii) the size of the step-free terrace. For small terraces and low deposition rates, deposited atoms migrate to the terrace boundaries before forming an island.

It is important to note that these observations are not the same as those made by previous authors, who argued that diffusion is in fact relatively isotropic at these temperatures. In particular, Bartelt et al. [79] observed fairly isotropic denuded zones following Si deposition at RT and annealing at 670°C. To address the apparent discrepancy between the observations of Bartelt et al. and those presented in Fig. 5.1, we now compare two different methods of promoting 2-D island growth. In method (1), we first deposit Si at 215°C, and then anneal the sample at 640°C. This procedure is essentially identical to that followed by Bartelt et al. In method (2), we simply deposit Si
at 640°C, i.e. similar to what was done in Fig. 5.1. Fig. 5.3 shows the results of this experiment. Figs. 5.3(a) and 5.3(b) show an initially step-free terrace following 2-D island growth using methods (1) and (2), respectively. It is clear from Fig. 5.3 that the denuded zone widths are quite sensitive to precisely how 2-D island growth is promoted. In particular, method (1) results in a denuded zone that appears relatively isotropic (Fig. 5.3(a)), whereas method (2) produces denuded zone widths that are quite anisotropic (Fig. 5.3(b)). The origin of this difference can perhaps be understood in terms of “instantaneous” vs. “continuous” Si deposition. In method (1), a certain amount of Si is effectively deposited instantaneously at the point when the temperature is brought up to 640°C from room temperature. Subsequent island formation therefore occurs under conditions of relatively large supersaturation (i.e., the difference between the actual adatom concentration and the equilibrium concentration), which in turn produces higher island density and small denuded zones. In method (2), on the other hand, Si is continuously deposited at 640°C, and island nucleation occurs in an environment where the steady-state supersaturation is relatively low, resulting in fewer islands and increased denuded zone widths.

5.4 Model

We now wish to obtain a quantitative relationship between the observed anisotropy in the denuded zone widths and the anisotropy in adatom diffusion. In the conventional approach developed by Mo et al. [77] and Villain et al. [78], nucleation theory is used to arrive at expressions for the denuded zone width $w$ of the form $w \propto D^\beta$, where $\beta = 1/6$ (1/4) for completely isotropic (anisotropic) diffusion. However, the analysis by Mo et al.
and Villain et al. rests on a number of assumptions that may not be valid for Si(001) at the temperatures used here. First, the contribution of the equilibrium adatom concentration $c_{eq}$ to the net adatom concentration during growth is neglected. However, LEEM studies by Theis et al. [80] indicate that $c_{eq}$ must be taken into account when using classical nucleation theory to describe island formation during Si(001) homoepitaxial growth. In fact, Theis et al. showed that the adatom concentration required for island nucleation differs by only a few percent from $c_{eq}$ at 650ºC, as mentioned above. Second, previous authors assumed “classical” Burton-Cabrera-Frank step-edge boundary conditions [66], i.e., that an adatom that reaches a step-edge immediately attaches to it. However, there exists strong evidence for the existence of a step attachment barrier on Si(001) [79]. Third, the analysis by Mo et al. and Villain et al. assume a critical island size of 1, i.e., that two joined adatoms form a stable island. However, Si(001) homoepitaxial growth studies indicate a critical island size of several hundred atoms at the intermediate temperatures considered in our work [80]. We therefore believe that a different approach is needed to relate the observed anisotropy in the denuded zone widths during Si(001) homoepitaxial growth to the anisotropy in adatom diffusion.

We now propose a simple model which can be used to relate the observed denuded zone widths with the diffusion anisotropy. Our model considers the time-evolution of the surface adatom concentration during the early stages of Si deposition, and relates the adatom depletion near the terrace boundaries to the adatom diffusion rates. Prior to island nucleation, the adatom concentration $c(x,y,t)$ on the terrace is given by [81]

$$D_{\parallel} \frac{\partial^2 c(x,y,t)}{\partial x^2} + D_{\perp} \frac{\partial^2 c(x,y,t)}{\partial y^2} + R = \frac{\partial c(x,y,t)}{\partial t}$$

(1)
where \( D_\parallel \) and \( D_\perp \) are the diffusion coefficients for adatom diffusion parallel and perpendicular to the surface dimer rows, respectively, and \( R \) is the Si deposition rate. Eq. (1) is subject to the following boundary conditions at the terrace boundary [81]:

\[
D_\parallel \frac{\partial c(x,y,t)}{\partial x} = \kappa_A [c(\pm L_\parallel / 2, y, t) - c_{eq}]
\]  

(2)

\[
D_\perp \frac{\partial c(x,y,t)}{\partial y} = \kappa_B [c(x,\pm L_\perp / 2, t) - c_{eq}]
\]

(3)

where \( \kappa_A,B \) determines the adatom attachment rate at single-height \( S_{A,B} \)-type step-edges, and \( c_{eq} \) is the equilibrium adatom concentration, i.e., the concentration at which there is no net movement of a (straight) step-edge. The step-edges at the boundary of the roughly square terrace are located at \( x = \pm L_\parallel / 2 \) and \( y = \pm L_\perp / 2 \), where \( L_\parallel \approx 6 \, \mu m \) and \( L_\perp \approx 5 \, \mu m \).

Eqs. (2) and (3) result from the need to balance the net diffusion current toward the step-edge with the net rate at which adatoms attach to the step-edge.

We have solved Eq. (1) subject to boundary conditions (2) and (3) numerically using the software program “FlexPDE”, using parameter values appropriate for Si(001) at 630°C. In our calculation, a Si flux \( R = 0.2 \) ML/min is turned on at time \( t = 0 \) sec. Prior to time \( t = 0 \) sec, the adatom concentration is assumed to take on the equilibrium value \( c_{eq} \approx 1.1 \times 10^{-2} \) ML everywhere on the terrace [63]. From previous measurements of the relaxation of lithographically defined macroscopic surface structures on Si(001) [82], we estimate that \( D_\parallel \) is on the order of \( 10^6 \, \text{nm}^2/\text{s} \) at the temperatures considered here. This value is consistent with the values used in Chapter 4. We find that the value \( D_\parallel = 6 \times 10^6 \) \( \text{nm}^2/\text{s} \) reproduces quite well the observed denuded zone widths \( w_\parallel \) in the direction parallel to the terrace dimer rows. \( D_\perp \) is an adjustable parameter in our model. From previous
measurements of the step mobility $\Gamma$ [79], we obtain [81] $\kappa_B \approx \kappa_A = \Gamma_A/a^4/c_{eq} \approx 4 \times 10^4$ nm/s, where $a = 0.543$ for Si. Note that if one assumes that the diffusing species is a dimer, one should use the value $a = 0.29$ nm, i.e., the square root of the dimer area. This analysis is not affected dramatically by the choice of $a$, and we expect the qualitative conclusions to remain valid. The calculation is propagated forward in time until a critical time $t_c$ when the maximum adatom concentration on the terrace has reached a critical concentration $c_c$, after which island nucleation is assumed to take place. From homoepitaxial Si(001) 2-D island growth experiments by Theis et al. [80] at similar temperatures to the ones used here, we estimate that $c_c/c_{eq} \approx 1.03$, which means that island nucleation occurs if the adatom concentration deviates only slightly from its equilibrium value. The value $c_c/c_{eq} \approx 1.03$ corresponds to a critical time $t_c \sim 0.1$ sec in our experiments. Note that we cannot observe island in LEEM until they reach a size of about 15-20 nm (after approximately 4 sec of exposure), and we cannot therefore directly verify whether island nucleation in fact occurs approximately 0.1 sec after turning on the Si flux.

Fig. 5.4 shows an example solution for the adatom concentration at time $t_c$. Fig. 5.4(a), which was obtained using $D_\parallel = 6 \times 10^6$ nm$^2$/s and $D_\parallel/D_\perp = 10$, shows a 2-D contour plot of the adatom concentration everywhere on the terrace. The contours are evenly spaced with a separation of 10% of the quantity $c_c/c_{eq} - 1$. Fig. 5.4(b) shows line profiles measured along the dotted lines in Fig. 5.4(a). We see that the adatom concentration is quite uniform everywhere on the terrace, except close to the terrace boundaries. This is consistent with our observation that the islands nucleate almost simultaneously across the terrace. The reduction in adatom concentration close to the terrace boundary gives rise to
the observed denuded zones. In particular, after the initial island nucleation, which occurs nearly uniformly everywhere on the terrace except close to the terrace boundaries, the newly formed islands act as sinks for subsequently deposited Si atoms. Hence, during subsequent Si deposition, all deposited Si atoms are incorporated into existing islands or the terrace boundaries. As a result, the number of island remains constant while the islands grow in size, and the observed denuded zone widths remain constant following initial island nucleation. Since we do not observe a strong reduction in island density and size immediately adjacent to the denuded zones, we expect the adatom concentration prior to initial island nucleation to be fairly constant everywhere on the terrace where islands eventually nucleates. Thus, we choose a critical adatom concentration $c_c$ above which island nucleation is assumed to occur which is close to the maximum adatom concentration ($1.03 \times c_{eq}$). In particular, we will define the denuded zone width to be the distance from the step-edge to the point on the terrace where the adatom concentration reaches 95% of $c_c$. Note that this value is somewhat arbitrary, and that this treatment only produces order-of-magnitude predictions. Thus, we expect islands to nucleate everywhere “inside” the 95% contour, whereas the region between the terrace boundaries and the 95% contour defines the denuded zones. We see from Fig. 5.4(b) that the calculated denuded zone width $w_\parallel$ in the fast diffusion direction is approximately 1.5 μm, in agreement with the observed value (Fig. 5.1(c)).

To compare our calculated adatom concentration profiles with the observed denuded zone widths at 630°C (Fig. 5.1(c)), we have produced plots similar to that shown in Fig. 5.4(a), but for several different values of $D_\parallel/D_\perp$. For each value of $D_\parallel/D_\perp$, we obtain a particular size and shape for the 95% adatom concentration contour. Three such 95%
contours (corresponding to $D_{\parallel}/D_\perp = 3, 10, \text{and } 20$) are superimposed on Fig. 5.1(c). As explained above, we expect the “correct” 95% contour to have the same shape as the roughly rectangular area in which islands have in fact formed. We see from Fig. 5.1(c) that the contour corresponding to $D_{\parallel}/D_\perp = 3$ is somewhat more square than the observed area in which islands form. On the other hand, the contours corresponding to $D_{\parallel}/D_\perp = 10$ and 20 both appear to have approximately the same rectangular shape as the island-covered area. In fact, for $D_{\parallel}/D_\perp$ much greater than 10, the calculated contours do not become significantly more rectangular with increasing $D_{\parallel}/D_\perp$. Since it is difficult to obtain an accurate measurement of the observed denuded zone width $w_\perp$ in the slow diffusion direction, we estimate from the above analysis a lower limit $D_{\parallel}/D_\perp \geq 10$ on the adatom diffusion anisotropy.

### 5.5 Summary and discussion

We have shown Si adatom diffusion on Si(001) surfaces to be anisotropic up to temperatures of at least 800$^\circ$C, the highest temperature available in our experiment. Hence, the suggestion by Tromp et al. that diffusion is fairly isotropic in this temperature regime doesn’t appear to be correct. The observed denuded zones are in agreement with the predictions of a simple model describing the (time-dependent) surface adatom concentration during the initial stages of Si deposition, from which we estimate that adatom diffusion at 630$^\circ$C is at least 10 times faster along the surface dimer rows than across them.

It is important to note that the observation in this chapter that Si adatom diffusion on Si(001) is anisotropic up to temperatures of at least 800$^\circ$C is not inconsistent with the
conclusions from chapters 3 and 4. In particular, the conclusion from chapter 3 that the electromigration force is a tensor that can have a sideways component with respect to the direction of the applied electric field was not dependent upon assuming isotropic diffusion. Rather, in chapter 3, electromigration was characterized by a mobility $\mu$ which contained the product of the diffusion coefficient $D$ and the adatom effective charge $q_{\text{eff}}$. The effect of assuming anisotropic diffusion would only be to change the magnitude of the principal components $\mu_\parallel$ and $\mu_\perp$, and would not change the basic conclusion in that chapter. Furthermore, in chapter 4, our modeling assumed isotropic diffusion and step properties, which may be a valid estimate at the high temperatures used there ($\sim 1000^\circ$C), since one generally expects surface anisotropies to diminish at higher temperatures. Without further modeling, however, it is not clear what the effects of assuming anisotropic diffusion and step properties would be on the quantitative conclusions reached in Chapter 3.
Fig 5.1. (a-d) Initially step-free Si terrace after deposition Si at a rate of .2 ML/min at 530, 600, 630, and 700°C. The denuded zone widths are anisotropic at all temperatures, indicating that adatom diffusion is also anisotropic.
Fig 5.2. LEEM image of the same terrace shown in Fig. 5.1, after depositing Si at a rate of .2 ML/min at 560°C for (a) 4 sec and (b) 16 sec. The island coverage and size distribution is fairly uniform across the surface after only a few seconds of Si growth (a), indicating that island nucleation occurred simultaneously across the terrace. Few or no additional islands nucleate during subsequent Si deposition (b).
Fig 5.3. LEEM images of a Si(001) surface after (a) depositing Si at 215°C, followed by annealing at 640°C (“method (1)”), and (b) depositing Si at 640°C (“method (2)”).
Fig 5.4. Calculated adatom concentration everywhere on the terrace at time $t_c$, when the maximum adatom concentration on the terrace has reached a critical concentration $c_c$. (a) Contour plot of the adatom concentration on the terrace. (b) Line profiles measured along the dotted lines in (a).
APPENDIX A

DESIGN AND CONSTRUCTION OF A 3-D MICROPOSITIONER

This appendix describes the design and construction of a micropositioner for use in ultra-high vacuum. The micropositioner offers sub-micron positioning accuracy in three dimensions, with a range of motion of approximately $1 \times 1 \times 1 \text{ mm}^3$. Motion in the horizontal (“xy”) plane is achieved by stacking two motion stages on top of each other, as illustrated in Fig. A.1. This design is based on a 2-D micropositioner proposed by Smith et al. Each motion stage consists of a stainless steel stage (Fig. A.1(b)) which is connected to a metal weight via a piezo-electric ceramic (PZT) tube. The piezo-tube is similar to those used in STM for sub-Å tip control. The motion stage rests on two quartz rods, which provide low-friction sliding contacts. The quartz rods mate with one V-groove and one rectangular groove on the bottom of the motion stage, so as to constrain the motion of the stage along one direction only. Motion of the stage is achieved by extending the piezo-tube quickly enough to overcome the static friction between the stainless steel stage and the quartz rods, and then by retracting the piezo-tube slowly to its starting position to avoid relative motion of the stage and the quartz rods. By stacking two such motion stages on top of each other, highly independent motion along the x- and y-directions is achieved.
To achieve motion in the vertical (z) direction, a novel “see-saw” micropositioner was implemented. The see-saw micropositioner is illustrated schematically in Fig. A.2. A stainless steel half-rod is seated onto two pairs of angled quartz rods. A piezo-electric driver assembly is attached to the stainless steel half-rod. The driver assembly consists of a macor rod with the element to be positioned attached to one end, and a weight connected to a piezo-tube on the other. The metallized piezo-tube has multiple electrodes on the outside of the tube to allow for vertical motion of the attached weight. Rotation of the driver assembly in the vertical plane is achieved by “throwing” the weight up or down by means of the piezo-tube so as to overcome the static friction between the stainless steel half-rod and the quart stands. The piezo-tube is then slowly retracted to its original position before taking the next step.

The complete assembled 3-D micropositioner is shown in Fig. A.3. The micropositioner is used to coarse position an STM tip assembly to within a few µm from the surface to be imaged. The micropositioner is mounted on a stainless steel base plate, which hangs from three Viton O-rings for vibration isolation. The O-rings hang from three threaded stainless steel rods, which in turn are attached to a 6” Conflat flange. This assembly was used successfully to image an evaporated gold surface on a Si(001) substrate (Fig. A.4).
Fig A.1. (a) Schematic view of 2-D micropositioner. (b) Dimensioned CAD drawing of top stage.
Fig A.2. Schematic view of the z-saw used for vertical positioning.
Fig A.3. The complete 3-D micropositioner.
Fig A.4. STM image of gold surface.
This appendix presents the Maple5 code used to calculate sublimation pit expansion
velocities and maximum pit radii for the experiments described in Chapter 4. For clarity,
the calculation is divided into 6 separated parts:

5.6 Solving for adatom concentrations

The adatom concentration on the inner ($r < r_1$) and outer ($r_1 < r < r_2$) is ‘c1’ and ‘c2’,
respectively. The code assumes that c1 and c2 have the forms shown in the code dump at
the end of this appendix, and then solves the boundary value problem. ‘Classic’ Burton-
Cabrera-Frank boundary conditions are used.

5.7 Input parameters

The calculation is performed at several different temperatures. A terrace is assumed
to be unstable against sublimation pit formation when the minimum adatom
concentration on the terrace reaches a fraction ‘c_min_over_c_eq’ of the equilibrium
adatom concentration. Although the only adjustable parameters that enter into the
calculation are the diffusion coefficient $D$ and the adatom lifetime $\tau$, the quantity ‘scale_lambda’ is introduced in the calculation for convenience. scale_lambda is a simple multiplicative factor for the product $\sqrt{D\tau} = \lambda$. Since the maximum pit size is mostly sensitive to $\lambda$, the maximum pit size predicted by the model can be changed by varying scale_lambda. In other words, scale_lambda imposes a constraint on the product $D\tau$.

‘scale_D’ is used to vary the value of $\tau$ (subject to the constraint imposed by scale_lambda) to match the pit expansion rate. It turns out that for all values of $c_{\text{min}}/c_{\text{eq}}$ less than about .995, both the maximum pit size and the pit expansion rate can be fitted independently using scale_lambda and scale_D. The remaining input parameters are of the form $\text{pre}_X \times \exp(E_X/kT)$, where ‘$X$’ denotes the input parameter.

5.8 Print some values of interest

As explained in Chapter 4, reasonable values of the input parameters should be used.

5.9 Calculate max size $w$ and step speed $v$

At each temperature, the maximum step size before a new pit nucleates is calculated. This is done by obtaining the diameter $w$ of the pit when the minimum adatom concentration on the terrace reaches the value $c_{\text{min}}/c_{\text{eq}} \times c_{\text{eq}}$. The step retraction rate for this maximum terrace size is then calculated. The calculation is performed both for the case of no added flux ($R = 0$), as well as for the case of an added flux ($R > 0$).
5.10 Plotting and writing data to file

The remaining code plots both the maximum pit size vs. temperature and step retraction speed vs. temperature for both $R = 0$ and $R > 0$, as well as the maximum pit size vs. step retraction speed. The data is written to file using standard C formatting code.

The following is a screen dump of the complete Maple code:
Solving for adatom concentrations

\( c_1: \)

\( \text{restart;} \)

\( c_1 := R \tau + A1 \text{Bessel} \left( 0, \frac{r}{\sqrt{Dd \tau}} \right) \)

Boundary condition:

\( \text{bc := } Dd \left( \frac{\partial}{\partial r} c_1 \right) \bigg|_{r = \frac{w}{2}} = \kappa \left( c_{eq} - c_1 \right) \bigg|_{r = \frac{w}{2}} \)

\( \text{solve(bbc), } \{A1\}; \)

\( \text{assign(%) ; } \) # assign the solution of the previous expression to A1

\( c_2: \)

\( c_2 := R \tau + A2 \text{Bessel} \left( 0, \frac{r}{\sqrt{Dd \tau}} \right) + B2 \text{BesselK} \left( 0, \frac{r}{\sqrt{Dd \tau}} \right) \)

Boundary conditions:

\( \text{bc1 := } Dd \left( \frac{\partial}{\partial r} c_2 \right) \bigg|_{r = \frac{w}{2}} = \kappa \left( c_{eq} - c_2 \right) \bigg|_{r = \frac{w}{2}} \)

\( \text{bc2 := } -Dd \left( \frac{\partial}{\partial r} c_2 \right) \bigg|_{r = \frac{w}{2}} = \kappa \left( c_{eq} - c_2 \right) \bigg|_{r = \frac{w}{2}} \)

\( \text{solve(} \{bc1,bc2\}, \{A2,B2\}; \)

\( \text{assign(%) ; } \)

Input parameters

'Internal' modeling parameters

\( \text{T_low := 1000 + 273: } \) # starting temperature

\( \text{T_inc := 5: } \) # temperature increment

\( \text{npoints := 11: } \) # number of points to calculate

Adjustable parameters

\( \text{unassign('T'): } \)

\( \text{c_min_over_c_eq := .8: c_min := c_min_over_c_eq * c_eq;} \)

\( \text{scale_lambda := .518: } \) # increase 'scale_lambda' to increase pit size w

\( \text{scale_D := .063: } \) # increase scale_D to
increase step speed

> E_D := 1.45:
> R2 := 0.0073 / a^2:  # deposition rate

Parameter sets that give good fits:

<table>
<thead>
<tr>
<th>E_D</th>
<th>c_min/c_eq</th>
<th>scale_lambda</th>
<th>scale_D</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45</td>
<td>.99</td>
<td>2.59</td>
<td>.29</td>
<td>.008</td>
</tr>
<tr>
<td>1.45</td>
<td>.9</td>
<td>.78</td>
<td>.92</td>
<td>.0075</td>
</tr>
<tr>
<td>1.45</td>
<td>.995</td>
<td>3.8</td>
<td>.42</td>
<td>.008</td>
</tr>
<tr>
<td>1.6</td>
<td>.997</td>
<td>5.1</td>
<td>2.2</td>
<td>.0075</td>
</tr>
<tr>
<td>2.0</td>
<td>.998</td>
<td>6.4</td>
<td>100.0</td>
<td>.007</td>
</tr>
<tr>
<td>1.45</td>
<td>.8</td>
<td>.518</td>
<td>.063</td>
<td>.0073</td>
</tr>
</tbody>
</table>

v2.08 parameter sets that give good fits:

<table>
<thead>
<tr>
<th>E_D</th>
<th>c_min/c_eq</th>
<th>scale_lambda</th>
<th>scale_D</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45</td>
<td>.999</td>
<td>7.97</td>
<td>.895</td>
<td>.008</td>
</tr>
<tr>
<td>1.45</td>
<td>.9</td>
<td>2.505</td>
<td>.28</td>
<td>.008</td>
</tr>
<tr>
<td>1.45</td>
<td>.90</td>
<td>.769</td>
<td>.089</td>
<td>.0075</td>
</tr>
<tr>
<td>1.45</td>
<td>.8</td>
<td>.518</td>
<td>.063</td>
<td>.0073</td>
</tr>
</tbody>
</table>

Old parameter sets that give good fits (with lambda_1003C = 14101):

<table>
<thead>
<tr>
<th>E_D</th>
<th>c_min/c_eq</th>
<th>scale_lambda</th>
<th>scale_D</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45</td>
<td>.90</td>
<td>.765</td>
<td>.115</td>
<td>.0073</td>
</tr>
<tr>
<td>1.45</td>
<td>.99</td>
<td>2.5</td>
<td>.36</td>
<td>.0077</td>
</tr>
<tr>
<td>1.45</td>
<td>.999</td>
<td>7.99</td>
<td>1.15</td>
<td>.0078</td>
</tr>
<tr>
<td>1.45</td>
<td>.8</td>
<td>.519</td>
<td>.082</td>
<td>.0073</td>
</tr>
<tr>
<td>1.45</td>
<td>.95</td>
<td>1.1</td>
<td>.161</td>
<td>.0077</td>
</tr>
</tbody>
</table>

v2.07:

<table>
<thead>
<tr>
<th>E_D</th>
<th>c_min/c_eq</th>
<th>scale_lambda</th>
<th>scale_D</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45</td>
<td>.99</td>
<td>2.5</td>
<td>.392</td>
<td>.0085</td>
</tr>
<tr>
<td>1.45</td>
<td>.8</td>
<td>.519</td>
<td>1.09e-1</td>
<td>.0095</td>
</tr>
<tr>
<td>1.45</td>
<td>.5</td>
<td>.278</td>
<td>.86e-1</td>
<td>~.0095</td>
</tr>
<tr>
<td>1.45</td>
<td>.999</td>
<td>7.99</td>
<td>1.24</td>
<td>.0085</td>
</tr>
<tr>
<td>1.45</td>
<td>.7</td>
<td>.405</td>
<td>.098</td>
<td>.0095</td>
</tr>
</tbody>
</table>

'Book' values:

> a := sqrt(.38*.76):
> k_B := .8614e-4:

1) Equilibrium adatom concentration:

> E_c_eq := .35: pre_c_eq := 1 / a^2:
> c_eq := pre_c_eq*exp(-E_c_eq/k_B/T):

2) Step kinetic parameter kappa:
E_Gamma := 1.369: pre_Gamma := 5.52e9:
> Gamma := pre_Gamma * exp(-E_Gamma/k_B/T):
> kappa := Gamma / c_eq / a^4:
> kappa0 := 1.9e13:
> E_kappa := 1.02:
> kappa := kappa0 * exp(-E_kappa/k_B/T):
>
3) Surface diffusion coefficient Dd:
> pre_D := scale_D*2e14:
> Dd := pre_D * exp(-E_D/k_B/T):
> D0 := 3.4e13:
> Dd := D0 * exp(-E_D/k_B/T):
>
4) Desorption lifetime tau:
> lambda_1003C := 12384: # size of pit is 12384 nm at T = 1003
> C (R = 0).
> #old: 14101
> Choose tau so that lambda = size of pit (for R = 0):
> E_tau := 4.0: pre_tau := lambda_1003C^2/eval(Dd, T = 1276)*exp(-E_tau/k_B/1276):
> tau := pre_tau*exp(E_tau/k_B/T):
> tau0 := 1/2.2e15:
> tau := tau0 * exp(E_tau/k_B/T):
>
Scale the diffusion coefficient Dd and lifetime tau by a factor 'scale_lambda':
> Dd := scale_lambda * Dd:
> tau := scale_lambda * tau:
>
Print some values of interest

> T := 1000 + 273: #T_low:
> 'a^2*D*c_eq' = a^2 * Dd * c_eq;
> 'D''/kappa''/lambda' = Dd/kappa/sqrt(Dd*tau);
> 'c_min/c_eq' = c_min_over_c_eq;
> D0 = scale_lambda*pre_D; 'E_D' = E_D;
> '1/tau0' = 1/scale_lambda/pre_tau; 'E_tau' = E_tau;
> kappa0 = pre_Gamma / pre_c_eq / a^4; 'E_kappa' = E_Gamma - E_c_eq;
> 'tau (T_low)' = tau;
> 'R' = R2*a^2;
> # R_max := c_min/tau*a^2; # - R_t; _R_t = R_t; _c_eq = c_eq;
> unassign('T'):

\[ a^2 D c_{eq} = 485046.6574 \]
\[
\frac{D}{\kappa \lambda} = .001016988340
\]
\[
\frac{c_{\text{min}}}{c_{eq}} = .8
\]
\[
D_0 = .65268 \times 10^{13}
\]
\[
E_D = 1.45
\]
\[
\frac{1}{\tau_0} = 1.887440389 \times 10^{16}
\]
\[
E_{\tau} = 4.0
\]
\[
\kappa_0 = .911357341 \times 10^{14}
\]
\[
E_{\kappa} = 1.019
\]
\[
\tau(T_{\text{low}}) = 3.682680616
\]
\[
R = .007300000000
\]

Calculate max size \( w \) and step speed \( v \)

Calculate max terrace width and step speed for \( R = 0 \) and \( R > 0 \)

\( R = 0 \)

\[
R_1 := 0; \ R := R_1;
\]
\[
\text{for } i \text{ to npoints do}
\]
\[
\ T := T_{\text{low}} + (i-1) \times T_{\text{inc}};
\]
\[
\ W := (184.4 \times 10^3 - 161.2 \times (T - 273)); \quad \# \text{ linear fit to observed values}
\]
\[
\ W := 1.85 \times \%;
\quad \# \text { approximate empirical relationship}
\]
\[
\text{sol := RootOf( eval(c1, r=0) = c_{\text{min}}, w, 1e3..1e5)};
\]
\[
\ w_{\text{max}}[i] := \text{evalf}(%);
\]
\[
\ v_a[i] := a^2 \times D_d \times (\text{eval(diff(c1,r), [r=%/2, w = %])} - \text{eval(diff(c2,r), [r=%/2, w = %])});
\]
\[
\ \text{Temp}[i] := T_{\text{low}} + (i-1) \times T_{\text{inc}} - 273;
\]
\[
\ text{od};
\]

\( R > 0 \)

\[
R := R_2;
\]
\[
\text{for } i \text{ to npoints do}
\]
\[
\ T := T_{\text{low}} + (i-1) \times T_{\text{inc}};
\]
\[
\ W := 715.1 \times 10^3 - 676 \times (T - 273);
\]
\[
\ W := 1.85 \times \%;
\]
\[
\text{sol := RootOf( eval(c1, r=0) = c_{\text{min}}, w, 1e3..1e5)};
\]
\[
\ w_{\text{max}}[i] := \text{evalf}(%);
\]
\[
\ v_b[i] := a^2 \times D_d \times (\text{eval(diff(c1,r), [r=%/2, w = %])} - \text{eval(diff(c2,r), [r=%/2, w = %])});
\]
\[
\ text{od};
\]
- **Plot data**

Prepare tables of observed values:

```maple
> Temp_obs[1]:=1003:Temp_obs[2]:=1009:Temp_obs[3]:=1015:Temp_obs
  [4]:= 1021:Temp_obs[5]:=1043:
>
> w_a_obs[1]:=12384:w_a_obs[2]:=11902:w_a_obs[4]:=10716:w_a_obs[5]
  :=8698: #w_a_obs[3]:=12202:
> v_a_obs[1]:=68.8:v_a_obs[2]:=79.2:v_a_obs[4]:=102.6:v_a_obs[5]
  :=162.6:v_a_obs[3]:=79.5:
  w_b_obs[4] := 13404:
  59.63: v_b_obs[4] := 77.16:
>
Plot calculated and observed values:

```maple
> wT_a_obs := [[Temp_obs[n],w_a_obs[n]] $n = 1..5]:
> wT_a := [[Temp[n],w_max_a[n]] $n = 1..npoints]:
> plot([wT_a,wT_a_obs], style = [line,point], color = [blue,red], symbol = [diamond,circle],
  title = `R = 0`, labels = [`T (C)`,'w (nm)`]);
>
> vT_a_obs := [[Temp_obs[n],v_a_obs[n]] $n = 1..5]:
> vT_a := [[Temp[n],v_a[n]] $n = 1..npoints]:
> plot([vT_a,vT_a_obs], style = [line,point], color = [blue,red], symbol = [diamond,circle],
  title = `R = 0`, labels = [`T (C)`,'v (nm/s)`]);
>
> wT_b_obs := [[Temp_obs[n],w_b_obs[n]] $n = 1..4]:
> wT_b := [[Temp[n],w_max_b[n]] $n = 1..npoints]:
> plot([wT_b,wT_b_obs], style = [line,point], color = [blue,red], symbol = [diamond,circle],
  title = `R > 0`, labels = [`T (C)`,'w (nm)`]);
>
> vT_b_obs := [[Temp_obs[n],v_b_obs[n]] $n = 1..4]:
> vT_b := [[Temp[n],v_b[n]] $n = 1..npoints]:
> plot([vT_b,vT_b_obs], style = [line,point], color = [blue,red], symbol = [diamond,circle],
  title = `R > 0`, labels = [`T (C)`,'v (nm/s)`]);
>
> wv_a_obs := [[v_a_obs[n],w_a_obs[n]] $n = 1..4]:
> wv_a := [[v_a[n],w_max_a[n]] $n = 1..npoints]:
> wv_b_obs := [[v_b_obs[n],w_b_obs[n]] $n = 1..4]:
```
wv_b := [[v_b[n], w_max_b[n]] $n = 1..npoints];
plot( [wv_a, wv_a_obs, wv_b, wv_b_obs], style = [line, point, line, point], color = [blue, red, blue, red], symbol = [diamond, circle, diamond, circle], title = `Max terrace width`, labels = [`v (nm/s)` , `w (nm)` ]);
Write data to file

```c
#t := "c_min = .8.txt";
t := "tmp.txt";

fd := fopen(t, WRITE);

fprintf(fd, "v2.11\n\n"):

fprintf(fd, "c_min/c_eq = %.3f\n\n", c_min_over_c_eq):

fprintf(fd, "E_D = %.2f eV\n\n", E_D):
fprintf(fd, "D0 = %1.1e nm2/s\n\n", pre_D*scale_lambda):

fprintf(fd, "E_tau = %.1f eV\n\n", E_tau):
fprintf(fd, "1/tau0 = %1.1e Hz\n\n", 1/(pre_tau*scale_lambda)):

fprintf(fd, "E_c_eq = %.2f eV\n\n", E_c_eq):
#fprintf(fd, "c_eq_0 = %.2f ML\n\n", c_eq_0):
fprintf(fd, "pre_c_eq = %g ML\n\n", pre_c_eq * a^2):

fprintf(fd, "(E_Gamma = %.2f eV )\n\n", E_Gamma):
fprintf(fd, "(pre_Gamma = %1.1e nm3/s )\n\n", pre_Gamma):
```
E_kappa = %.2f eV
kappa0 = %1.1e nm/s
a = %.2f nm
R = %g ML/s
scale_lambda = %.3f
scale_D = %g
npoints = %d
T_low = %d K
T_inc = %d K
lambda_1003C := %f

tru := 1:
if (tru = 1) then
   R_dep 	Temp 	v 	w_max 
   for i to npoints do
      if (type(w_max_a[i], float) and type(v_a[i], float)) then
         fprintf(fd, "%0.4f \t%d \t%4.1f \t%.2f 
", R1 * a^2, Temp[i], v_a[i], w_max_a[i]/1000);
      else fprintf(fd, "N/A \tN/A \tN/A \tN/A 
"):
   fi:
   od:
   fprintf(fd, "\n"):
   for i to npoints do
      if (type(w_max_b[i], float) and type(v_b[i], float)) then
         fprintf(fd, "%0.4f \t%d \t%4.1f \t%.2f 
", R2 * a^2, Temp[i], v_b[i], w_max_b[i]/1000);
      else fprintf(fd, "N/A \tN/A \tN/A \tN/A 
"):
   fi:
   od:
   fi:
   fclose(fd):
LIST OF REFERENCES


