HALOGEN-INDUCED MODIFICATION OF SILICON SURFACES: ETCHING ROUGHENING, AND STEP TRANSFORMATIONS

BY

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DISSERTATION

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ABSTRACT

I have combined scanning tunneling microscopy with density functional calculations and Monte Carlo simulations to investigate halogen-induced modifications of Si surfaces, including etching, roughening and step transformations. These investigations have focused on elucidating the atomic-level details associated with the evolution of terrace and step sites on Cl-Si(100)-(2x1) under conditions of halogen supersaturation. I present a novel adsorption mechanism that is accessed upon exposing nearly-saturated Cl-Si(100)-(2x1) to a flux of Cl\textsubscript{2}, whereby dangling bonds of the nearly-saturated surface mediate the insertion of Cl adsorbates into non-equilibrium adsorption sites. The adsorbates are kinetically trapped within these sites due to energy constraints and lack of available and more favorable adsorption sites. Inserted Cl adsorbates force the surface to evolve along a novel etching pathway at elevated temperature resulting in dimer vacancy formation without the customary Si regrowth features attributed to halogen etching processes. This process is investigated at 700 – 825 K and the reaction mechanism is extracted from analysis of the appropriate rate equations.
To my grandfather, Edmund C. Cooke
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# TABLE OF CONTENTS

## CHAPTER 1 SYNOPSIS .................................................................................................................. 1

1.1 Background .............................................................................................................................. 1
1.2 Overview .................................................................................................................................. 3
1.3 References ............................................................................................................................... 10
1.4 Tables .................................................................................................................................... 11
1.5 Figures ................................................................................................................................... 12

## CHAPTER 2 PHONON-ACTIVATED ELECTRON-STIMULATED DESORPTION OF HALOGENS FROM Si(100)-(2x1) ......................................................... 14

2.1 Introduction ............................................................................................................................. 14
2.2 Experiment ............................................................................................................................... 15
2.3 Results and discussion ............................................................................................................ 15
2.4 Conclusions ........................................................................................................................... 18
2.5 References ............................................................................................................................. 19
2.6 Tables .................................................................................................................................... 20
2.7 Figures ................................................................................................................................... 21

## CHAPTER 3 Cl INSERTION ON Si(100)-(2x1): ETCHING UNDER CONDITIONS OF SUPER-SATURATION ................................................................. 23

3.1 Introduction ............................................................................................................................. 23
3.2 Experiment ............................................................................................................................... 24
3.3 Results and discussion ............................................................................................................ 25
3.4 Conclusions ........................................................................................................................... 31
3.5 References ............................................................................................................................. 31
3.6 Figures ................................................................................................................................... 34

## CHAPTER 4 ATOMIC PROCESSES DURING Cl SUPERSATURATION ETCHING OF Si(100)-(2X1) ......................................................................................... 40

4.1 Introduction ............................................................................................................................. 40
4.2 Experiment ............................................................................................................................... 41
4.3 Results and discussion ............................................................................................................ 42
4.4 Conclusions ........................................................................................................................... 49
4.5 References ............................................................................................................................. 51
4.6 Figures ................................................................................................................................... 54
CHAPTER 5  ADSORBATE-MEDIATED STEP TRANSFORMATIONS AND TERRACE REARRANGEMENT OF Si(100)-(2X1) .............................59

5.1 Introduction .....................................................................................59
5.2 Experiment ......................................................................................60
5.3 Results and discussion .....................................................................61
5.4 Conclusions .....................................................................................66
5.5 References .......................................................................................67
5.6 Figures .............................................................................................70

CHAPTER 6  COVERAGE-DEPENDENT CHEMISORPTION OF Cl ON Si(114) ..........................................................73

6.1 Introduction .....................................................................................73
6.2 Experiment ......................................................................................74
6.3 Results and discussion .....................................................................75
6.4 Conclusions .....................................................................................80
6.5 References .......................................................................................80
6.6 Tables ..............................................................................................82
6.7 Figures .............................................................................................83

CHAPTER 7  ADSORBATE-INDUCED ROUGHENING OF Si(100) BY INTERACTIONS AT STEPS .........................................88

7.1 Introduction .....................................................................................88
7.2 Experiment ......................................................................................89
7.3 Results and discussion .....................................................................91
7.4 Conclusions .....................................................................................94
7.5 References .......................................................................................95
7.6 Figures .............................................................................................97
CHAPTER 1

SYNOPSIS

1.1 Background

The interaction of halogen adsorbates with Si surfaces has been widely studied due to the widespread use of halogen-based plasmas in the fabrication of Si-based electronic devices. Earlier studies concentrated on halogen adsorption, surface chemistry, and the nature of the species liberated from the surface [1-4]. More recently, scanning tunneling microscopy (STM) has been used to investigate the halogen etching process and resulting surface modification with atomic-level detail [5-8].

STM studies combined with theoretical calculations have elucidated the atomic-level sequence of events that occur during halogen etching of Si(100). de Wijs et al. utilized first-principles local-density-functional-theory (DFT) to obtain the dark potential energy surface in Fig. 1.1 for Cl-Si(100) and the associated energies leading to SiCl₂ desorption [9]. The process begins with an isomerization reaction that converts a Si dimer terminated with halogen adsorbates, 2SiX, into SiX₂ + Si. To prevent the reverse reaction from occurring, the so-called Si bystander escapes onto the terrace leaving behind a single Si vacancy. The volatile SiX₂ specie desorbs upon surmounting a desorption barrier of 3.1 eV. With such a large activation barrier, the escape of the Si bystander onto the terrace is a critical to the etching process by preventing the reverse isomerization reaction from occurring. Furthermore, de Wijs et al. calculated that the Si bystander’s rate of escape is enhanced by the presence of neighboring halogen-free sites.
to which it can attach. Indeed, STM and TPD investigations confirm that the etch rate of Cl-Si(100)-(2x1) has a maximum at $\theta_{\text{Cl}} = 0.8$ ML and approaches zero at higher coverages [6, 10].

Both the isomerization reaction, 2.1 eV, and the escape of the Si bystander, 2.4 eV, were found to have significantly lower activation barriers than that for desorption, 3.1 eV. At temperatures below those necessary to activate SiX$_2$ desorption, Nakayama et al. [7] reported the observation of surface modification without material removal and proposed the reaction pathway depicted by the light potential energy surface in Fig. 1.1. This pathway branches off of that associated with halogen etching prior to the loss of SiX$_2$ but following the escape of the Si bystander. Without sufficient thermal energy to surmount the desorption barrier, the SiX$_2$ specie decays by transferring its halogen adsorbates onto neighboring halogen-free sites and the remaining Si atom escapes onto the terrace. This process generates dimer vacancies and Si regrowth features similar to those observed during etching, except Si and Cl are not lost during this process. Once again, halogen-free terrace dimers are required for this roughening reaction to occur.

Several studies have combined STM and DFT to establish the driving force behind the roughening reaction [11-14]. The proposed models and their shortcomings are discussed in further detail in Chapter 7. Boland and co-workers [11, 12] first proposed lateral steric repulsive interactions between adjacent halogen adsorbates as the driving force for roughening. The interactions that were considered ($\alpha$, $\beta$, and $\gamma$) are reproduced in Fig. 1.2 [12], and the calculated energies are tabulated in Table 1.1 [11]. The reduction of steric repulsion was argued to offset the energy incurred by the formation of steps associated with dimer vacancies and Si regrowth features. However, the steric
interaction model could not account for the observed roughening at low halogen coverages [8, 15], in which case the abundance of halogen-free sites permits the distance between neighboring adsorbates to be maximized. Chen and Boland countered this discrepancy by proposing their anti-correlated dimer interaction [14, 15], depicted in Fig. 1.3. According to this model, there is an attractive interaction amongst adjacent halogen-free dimers associated with their out-of-phase buckling. This interaction nearly compensates the steric repulsion of adjacent Cl adsorbates and fosters the formation of adsorbate patches. Once assembled into patches, steric repulsion of adjacent Cl adsorbates will induce roughening as in Ref. 12. This cyclic argument fails to correctly identify the driving force for roughening and a more plausible model is discussed in Chapter 7.

These studies have identified the sequences of events involved in and the forces that are responsible for halogen-induced surface modification and etching of Si(100)-(2x1). However, these studies were restricted to monolayer and sub-monolayer halogen coverages, as it was previously accepted that the halogen coverage could not exceed 1 ML [5-8]. As presented in this dissertation, it is indeed possible to achieve a halogen coverage in excess of 1 ML, and the resulting supersaturated state of Si(100) provides access to previously unobserved and novel etching mechanisms.

1.2 Overview

My research expands upon the current understanding of fundamental processes and atomic-level pathways associated with halogen-induced modification of Si surfaces
and extend this knowledge into a previously unexplored regime of halogen surface coverage. A brief synopsis of the chapters detailing these studies is presented below.

Chapter 2 presents the process of spontaneous halogen desorption that is ultimately responsible for producing the dangling bonds that mediate the insertion of halogen atoms at elevated temperatures. Halogen-free, or bare, surface sites are necessary to initiate the conventional etching and roughening reactions on halogen-terminated Si(100) [5-10]. However, Xu et al. reported that roughening will occur on fully Cl-terminated Si(100) after an initial lag period at 700-750 K [8, 15]. This onset of roughening indicates the presence of bare sites at temperatures well below the Cl₂ desorption peak, as determined by temperature programmed desorption experiments [1].

To investigate the creation of bare sites on Cl-, Br-, and I-Si(100), STM was utilized to monitor the evolution of the surface after heating. The observance of single adsorbate vacancies permitted the determination that the requisite bare sites were created by spontaneous desorption of single halogen adsorbates [16]. An Arrhenius plot of the Cl revealed kinetic parameters that were far less than those expected from thermally activated desorption. Furthermore, the activation energy for the desorption process changed with the position of the Fermi level. An in-depth analysis of the prefactor determined that Br desorption involved an electronic transition from bulk Si into the Si-Cl* and Si-Br* anti-bonding states. Moreover, this transition was found to be mediated by optical phonons of the Si lattice, for which the term phonon-activated, electron-stimulated desorption (PAESD) was coined.

The activation energy for Cl desorption was found to be 2.26 ± 0.0.08 eV, which corresponds well to the energy difference between the Fermi level, E = 0.10 eV, and the
Si-Cl* anti-bonding state, \( E = 2.26 \, \text{eV} \). The activation energy for Br desorption was found to be \( 1.23 \pm 0.08 \, \text{eV}, 0.84 \pm 0.09 \, \text{eV}, \) and \( 0.05 \pm 0.11 \, \text{eV} \) for p-Si, low-doped n-Si, and heavily-doped n-Si, respectively. Desorption rates for I were nearly three orders of magnitude larger than that for Cl and Br. Since the Si-I* antibonding states overlap with the conduction band minimum, conduction-band electrons are readily available to be captured by those antibonding states, resulting in the much higher desorption rate for I.

Chapter 3 presents the mechanism for halogen insertion leading to a novel etching pathway that is accessible under condition of halogen supersaturation. It was well accepted that the Cl coverage \( (\theta_{\text{Cl}}) \) on Si(100)-(2x1) saturated at 1 ML with each DB terminated with Cl [17]. The discovery of single DB creation on Cl- and Br-Si(100) at elevated temperatures via PAESD hinted at the possibility achieving supersaturation, i.e. \( \theta_{\text{Cl}}, \theta_{\text{Br}} > 1 \, \text{ML} \), through an abstraction and insertion mechanism found to occur on Si(100) after exposure to F\(_2\) [18]. Previous reports of Cl adsorption into a Si-Si dimer bond after exposure to Cl\(_2\) at 140 K suggested that such an insertion mechanism is plausible [4].

To investigate insertion and its implications on etching, we exposed fully Cl-terminated Si(100) to varying fluxes of Cl\(_2\) while keeping the sample at a constant elevated temperature, \( T \geq 750 \, \text{K} \) [19]. The resulting surfaces were composed simply of dimer vacancy lines elongated along the dimer row direction with occasional branching events. Surfaces prepared under similar conditions and heated in the absence of an impinging Cl\(_2\) flux were characterized by dimer vacancy lines and etch pits accompanied by Si regrowth chains and islands. The absence of Si regrowth features and the lack of
bare sites to activate the conventional etching pathway suggest that etching under conditions of supersaturation proceeds along a novel etching pathway.

The supersaturation etching (SSE) pathway was presumed to involve insertion of Cl into Si-Si surface bonds forming Cl(i) moieties, diffusion and pairing of Cl(i) to form 2SiCl₂, and ultimately desorption of SiCl₂. A plot of the SSE etch rate as a function of Cl₂ flux in the range 750-825 K revealed the presence of a flux independent regime at each temperature point. This indicated that Cl₂ does not directly insert into the surface. Instead, insertion must be mediated by a special surface site. It is shown in Chapter 2 that spontaneous desorption of Cl adsorbates occurs on Cl-Si(100) at elevated temperatures via PAESD. The DBs created are capable of inducing dissociation and insertion. An Arrhenius plot of the SSE etch rate yields an activation energy, 2.27 ± 0.04 eV, in excellent agreement with that of PAESD, 2.26 ± 0.05 eV. This implied that DB creation via PAESD is the rate limiting step in the SSE process.

Chapter 4 provides evidence for the presence of inserted Cl atoms on Cl-Si(100) in the form of bright features and identifies their role in the SSE process. During SSE, a previously unobserved surface species, the so-called bright feature (BF), is generated and visible in filled-state STM images [19]. BFs were believed to be associated with Cl(i), although a direct correlation had not been established. To correctly identify the BF, a surface with 0.97 ML of Cl (0.03 ML BDs) was prepared and then further exposed this surface at room temperature to ~0.1 ML of Cl₂ [20]. This produced a surface with 0.067 ML of BDs and 0.024 ML of BFs. The surface was then annealed at 650 K for 5 min to facilitate diffusion of the presumed Cl(i) species. The concentration of both BDs and BFs decreased in an approximate 1:1 relationship as a result of annealing. Since each BD
contains two DBs it was determined that BFs must contain at least two Cl(i), since the possibility that some BFs may contain more than two Cl(i) cannot be ruled out.

According to the SSE pathway proposed in Chapter 3, species e is the only species that contains two Cl(i). If it corresponds to the BF, an Arrhenius plot of the BF concentration should give the difference in activation energies for Cl insertion and etching of a single SiCl₂. In the range 750-825 K, an activation energy of 0.2 eV is obtained, making the etching activation energy ~2.5 eV. Total energy calculations by de Wijs et al. [9] determined the desorption barrier for the first SiCl₂ of species e to be 1.4 eV, but 2.5-2.9 eV for the second. Even at 600 K, species e will readily lose a SiCl₂ unit and convert to g. Its short lifetime precludes it from being observed by STM, and we eliminate it as a possible BF candidate. Since no other species within the proposed SSE pathway contains two Cl(i), the pathway must include another as-of-yet unidentified species that is a precursor to species e. The SSE pathway then follows a pathway in which two Cl(i) in close proximity to one another form a stable complex and must overcome a ~2.5 eV barrier to pair and form species e. Along with identifying the origin of the BF, this study also demonstrated that Cl insertion is not restricted to SSE, i.e., elevated temperatures and saturated surfaces. Insertion occurs at room temperature and paired DBs of BDs mediate this process as well.

Chapter 5 discusses the implications of inserted halogen atoms on step sites and the step structure of Cl-Si(100)-(2x1) at 700 and 725 K. In this temperature range, Cl(i) becomes increasingly hindered from overcoming the significant 2.5 eV barrier to produce SiCl₂ species and continue to diffuse about the surface. The observance of single-atom-wide vacancies along Sₐ steps suggest that Cl(i) accumulates at step sites. First principle
density functional theory calculations reveal a stable adsorption site at r-S_B steps that is ~0.5 eV lower in energy than those reported for Cl(i) on the terrace. Further calculations reveal the probable reaction mechanism and atomic-level sequence of events associated Si rebonded atom etching that agree with experimental observations. A careful rate analysis confirms the increase in step etching at lower temperatures is a result of an increased concentration of Cl(i) at the step. The resulting step structure undergoes further transformation as rebonded atom vacancies diffuse onto the terrace and steps retreat. These observations reveal that steps are much more dynamic at saturated and supersaturated halogen coverages.

Chapter 6 investigates the dissociative chemisorption of Cl\textsubscript{2} on Si(114)-(2x1). Si(114) is a stable, planar, high-index surface possessing similar surface components to the more familiar Si(100) [21]. It can be thought of as a highly-stepped (100) surface composed of 1 dimer-wide terraces separated by bi-atomic height steps. The surface consists of three basic units: rebonded atoms, dimers, and tetramers. The dimer and rebonded atom units comprise a rebonded, double-height B step (r-D\textsubscript{B}) and the tetramer a non-rebonded, double-height B step (n-D\textsubscript{B}) in relation to Si(100). Since non-rebonded B steps are rarely observed on Si(100), an investigation of Cl adsorption on Si(114) allows us to gain insight into the interaction of halogens with the non-rebonded step structure.

STM images revealed preferential adsorption of Cl on rebonded atoms, followed by dimers, and lastly tetramers. The equilibrium distribution of Cl reflected the preservation of \pi-bonds attributed to the dangling bonds of the (114) reconstruction. Moreover, the dissociative chemisorption of Cl\textsubscript{2} was sufficiently exothermic that the resulting Cl atoms were able to interrogate the potential energy landscape to find local
energy minima for adsorption. An analysis of the resulting chemisorption sites on the
tetramer units revealed configurations that reflected the $\pi$-bonding predicted along each
arm and along the dimer bond direction.

Chapter 7 identifies an overlooked adsorbate-substrate interaction, termed
preferential step adsorption interaction (PSAI), that is determined to be the driving force
for halogen-induced surface modification of Si(100)-(2x1) in the low coverage regime.
Previous models of surface roughening have been unable to account for the observance of
large pits and regrowth features at adsorbate coverages below 0.50 ML. PSAI is manifest
in the observation of preferential adsorption of Cl adsorbates at rebonded step sites. An
analysis of acquired STM images of the equilibrium distribution of Cl adsorbates on
Si(100) after annealing at 650 K revealed a terrace site occupancy of 0.12 ± 0.01,
whereas the occupancy of rebonded atoms was an astounding 0.65 ± 0.07. Since the
equilibrium Cl occupancy of distinct surface sites is related to the difference in
adsorption energies, an adsorption energy difference of 0.14 ± 0.02 eV at 650 K was
deduced. The inclusion of PSAI of 0.14 eV into Kinetic Monte Carlo simulations
produced a surface with significantly greater modification of the substrate that more
closely resembled what is observed experimentally.
1.3 References


1.4 Tables

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<th>Intra-row $\alpha$ (meV)</th>
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<tr>
<td>Fluorine</td>
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Table 1.1 The $\alpha$ and $\beta$ steric repulsive energies calculated with DFT for Br, Cl and F. The $\gamma$ interaction was found to be negligible.
1.5 Figures

Figure 1.1 Potential energy surface for X-Si(100). The dark pathway corresponds to thermally-activated material removal by SiX$_2$ desorption, with SV and DV denoting single and dimer vacancies. Si(a) is a Si adatom on the terrace, produced by vacancy formation. The light branch describes the decay of SiX$_2$ by transfer of the halogens to nearby bare Si dimers. It leads to a dimer vacancy, regrowth Si, and the recycling of halogens. Both pathways are blocked for saturated surfaces because there are no sites that can accommodate Si(a) atoms.
Figure 1.2 Steric repulsive interactions between adsorbed halogen atoms on Si(100)-(2x1).

Figure 1.3 Supercells used by the authors of Ref. 13 to compute the patch-formation energy. (Right) 2 adsorbate-terminated dimers separated by bare dimers. (Left) 2 adsorbate-terminated dimers adjacent to one another.
CHAPTER 2

PHONON-ACTIVATED ELECTRON-STIMULATED DESORPTION OF HALOGENS FROM Si(100)-(2x1)

2.1 Introduction

Halogen-free Si sites are required for conventional halogen etching of Si(100)-(2x1) to commence [2]. However, investigations into the etch rate dependence on halogen surface coverage revealed that etching proceeds on fully saturated Cl-Si(100)-(2x1) following a high-energy kinetic step [3, 4].

In this chapter, the high-energy kinetic step that permits halogen etching to commence at saturation coverages is identified and discussed. It is shown that spontaneous desorption of single halogen adsorbates produces the necessary halogen-free sites to initiate the etching process. A thorough investigation into the desorption mechanism, including rate analysis, revealed a novel desorption process that involves both thermal excitation and electronic stimulation, for which the term phonon-activated, electron-stimulated desorption (PAESD) was given [5]. The PAESD process is essential to supersaturation etching, as discussed in Chapter 3, which serves as the basis for the work presented within this dissertation, thus necessitating its discussion.

2.2 Experiment

From Ref. 1, “the experiments were carried out in an ultrahigh vacuum system with a base pressure of 4x10^{-11} Torr. The Si wafers were p-type (B doped, \(~0.010\ \Omega\text{-cm\ corresponding to } 7x10^{18} \text{ cm}^{-3}, \) denoted p-Si) and n-type (P doped, \(~0.5\ \Omega\text{-cm, } 9x10^{15} \text{ cm}^{-3}, \) denoted ldn-Si for lightly-doped n-Si and \(~0.005\ \Omega\text{-cm, } 1x10^{19} \text{ cm}^{-3}, \) denoted hdn-Si for heavily-doped n-Si). Clean surfaces were prepared using thermal treatments [6] and imaged with a scanning tunneling microscope (STM) to verify surface quality. They were then exposed to a flux of Cl\(_2\) or Br\(_2\) to achieve surface saturation, defined as one halogen atom bonded to each dangling bond (DB) of the (2x1) surface. Thereafter, they were heated to a specific temperature in the range 620 – 800 K for a specific time in the range 1 – 90 min, cooled rapidly, and imaged at room temperature [7]. The amount of halogen lost was determined from the number of bare sites per unit area [8]. The imaging conditions had no effect on the halogen concentration, as concluded from repetitive same-area scanning.”

2.3 Results and discussion

Figure 2.1(a) is an STM image of Si(100)-(2x1) after a saturation exposure to Cl\(_2\). Si dimer rows run diagonally across the image and each Si atom of a surface dimer is terminated with a Cl adsorbate. A single dimer vacancy (DV) is identified in the lower left corner and is the only identifiable defect in the image. Figure 2.1(b) shows the surface of Fig. 2.1(a) after a 20 min anneal at 750 K. Bare dimers (BDs) are now evident and indicative of Cl loss [8]. The amount of DVs did not increase as a result of the anneal indicating that halogen desorption is the only reaction that has occurred.
The change in the number of BDs, or similarly the change in halogen coverage, can be related to the activation energy for desorption through a first order rate equation. The rate of a first order desorption reaction is given as

\[ r = -\frac{d\theta}{dt} = k\theta \]  

(2.1)

where \( k \) is the rate constant, \( \theta \) is the reactant (halogen) concentration, and \( t \) is time.

The rate constant can be written as

\[ k = \nu \exp \left( -\frac{\epsilon}{k_B T} \right) \]  

(2.2)

where \( \nu \) is the prefactor, \( \epsilon \) is the activation energy for desorption, \( k_B \) is the Boltzmann constant, and \( T \) is temperature. Substituting Eq. 2.2 into Eq. 2.1 gives

\[ \ln k = \ln \left( \frac{\theta_i}{\theta_f} \right) \frac{1}{t} \ln \left( \frac{\theta_i}{\theta_f} \right) = -\frac{\epsilon}{k_B T} + \ln \nu \]  

(2.3)

The significance of Eq. 2.3 is that \( \theta_i \), \( \theta_f \), and \( t \) are experimentally accessible parameters. A simple count of the number of BDs in images equivalent to Fig. 2.1(b) are sufficient to obtain \( \theta_i \) and \( \theta_f \) before and after a given anneal at temperature \( T \) for length of time \( t \). An Arrhenius plot will determine the activation energy for desorption and give insight into the desorption process itself.

An Arrhenius plot incorporating the Cl desorption parameters is given in Fig. 2.2(a) using Eq. 2.3. Results from Br [5] and I [1] experiments are also included for comparison. However, the discussion of I desorption is left to Ref. 1. The activation energies and prefactors determined from straight-line fits are given in Table 2.1. The desorption rates are nearly the same for Cl and Br in the range 700 - 800 K.
A previous investigation of Br desorption determined that the activation energy for desorption was dependent upon the doping level of the Si substrate [5]. The level of doping ultimately affects the location of the Fermi level with respect to the valence band maximum (VBM). Significantly, the change in the Fermi level with respect to the VBM was found to be in excellent agreement with the change in activation energy for Br desorption. This discovery pointed toward an electronic excitation in the Si-Br $\sigma^*$ state.

From Ref. 1, “Fig 2.2(b) shows a schematic band diagram for Si(100) with the relevant energy levels at 700 K. The double-headed arrows in Fig. 2.2(b) show the excitation energies for Cl, Br, and I desorption from the three types of samples. As shown, the Fermi level is about 0.10 eV above the VBM for p-Si, 0.48 eV above the VBM for ldn-Si, and 0.82 eV above the VBM for hdn-Si at 700 K, assuming non-degenerate doping. Significantly, these Fermi level shifts associated with doping are in excellent agreement with the changes in the activation energies for Br desorption. This implies that in all three cases the electrons are being excited into the same state which we have proposed to be the Si-Br $\sigma^*$ state [5].

“Table 2.1 shows that the prefactors found from the Arrhenius plots of Fig. 2.2(a) vary over many orders of magnitude as the activation energies increase from Br on hdn-Si to Cl on p-Si. The observation that an increase in activation energy is accompanied by an exponential increase in the prefactor is well known from the literature of biological, chemical, and physical processes as the compensation effect or Meyer-Neldel (MN) rule [9-12]. Quantitatively, the MN rule relates the prefactor and activation energy for a family of processes through $\ln \nu = a + bE$ where $a$ and $b$ are constants. Yelon and they showed that the inverse of the slope, $\Delta_0 = \frac{1}{b}$, is a characteristic energy that provides an
order of magnitude estimate of the elementary excitations [13, 14]. For Br-Si(100), the
best fit to the Meyer-Neldel plot (ln v vs. ε) gives Δ₀ = 60 ± 5 meV, implicating optical
phonons of the Si lattice as the energy bath [15].”

Figure 2.3 is a Meyer-Neldel plot based on the results of Fig. 2.2(a). Remarkably,
the datum point for Cl-p-Si falls in line with the Br desorption data. This increases the
energy and the prefactor scales substantially and an overall best fit of Δ₀ = 66 ± 5 meV is
obtained. According to the YM model, processes with activation energies that lie on the
same MN line belong to the same family of processes that have the same energy bath and
coupling to that bath. From Ref. 1, “the fact that the Cl and Br data fall in line shows that
the phonon spectrum and the electron phonon coupling are similar for Br and Cl, as
would be expected due to the similarity of the Si-halogen bonds.” It is interesting to note
that the activation energy for Cl desorption is 1 eV larger than that for Br desorption.
This is consistent with the greater binding energy of Cl on Si(100)-(2x1) which is
expected to produce a larger separation between the Si-Cl antibonding states and the
Fermi level. Thus, it can be concluded that Cl desorption occurs via PAESD.

2.4 Conclusions

The results of this investigation demonstrate the generation of DBs from
spontaneous desorption of halogen adsorbates via PAESD on Cl-saturated Si(100)-(2x1).
These DBs are essential to etching and roughening reactions on fully saturated surfaces.
As will be discussed in Chapters 3 and 4, these DBs also mediate Cl₂ dissociation and Cl
insertion into Si-Si surface bonds leading to Cl coverages in excess of 1 ML and,
ultimately, provide access to a novel etching pathway.
2.5 References


7. The temperature was monitored with an optical pyrometer calibrated with a W-Re thermocouple; heating rate ~3 K s\(^{-1}\); reproducibility ± 5 K.

8. G.J. Xu, E. Graugnard, B.R. Trenhaile, Koji S. Nakayama, and J.H. Weaver, Phys. Rev. B 68, 075301 (2003). For Cl-Si(100) at a sample bias of -0.8 V, the BD appears much brighter than the two dimers on either side while for Br-Si(100) at a sample bias of -0.6 V, the two dimers on either side appear brighter than the BD.


15. Yelon _et al._ in Ref. 30 fitted data for deep trapping in crystalline silicon and found a \( \Delta_0 \) value of 50 ± 25 meV. They also showed that values of \( \Delta_0 \) in the range of 35-70 meV are plausible for coupling to optical phonons for semiconductors with bandgaps of 1-2 eV. For comparison, \( \Delta_0 \) values of <1 meV would be expected for coupling to acoustical phonons.

### 2.6 Tables

<table>
<thead>
<tr>
<th>Halogen (Substrate)</th>
<th>Activation Energy ( \Delta E(eV) )</th>
<th>Prefactor ( \nu(s^{-1}) )</th>
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<tr>
<td>Cl (p-type)</td>
<td>2.26 ± 0.08</td>
<td>( 1 \times 10^{10.0\pm1.0} )</td>
</tr>
<tr>
<td>Br (p-type)</td>
<td>1.23 ± 0.08</td>
<td>( 10^{4.0\pm0.5} )</td>
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<tr>
<td>Br (Iln-type)</td>
<td>0.84 ± 0.09</td>
<td>( 10^{1.0\pm0.5} )</td>
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<tr>
<td>Br (hdn-type)</td>
<td>0.50 ± 0.11</td>
<td>( 6 \times 10^{-2.0\pm0.9} )</td>
</tr>
</tbody>
</table>

Table 2.1 Thermodynamic properties of the desorption reactions, excited by the optical phonons of Si. The activation energies and prefactors were found from the Arrhenius plots of Fig. 2.2(a).
2.7 Figures

Figure 2.1  Filled-state scanning tunneling micrographs (100x100 Å$^2$) of Cl on p-type Si(100)-(2x1) acquired at room temperature with a sample bias of -1.1 and -1.0 V for (a) and (b), respectively. Dimer vacancies (DVs) appear in each image as dark dimer-sized features. The bare dimers (BDs) appear as bright features involving three dimers and the middle dimer appears significantly brighter than the two dimers on either side. (a) The initial Cl coverage was 0.999 ML, (b) The sample was heated to the temperature indicated for the time given. The final Cl coverage was 0.989 ± 0.003 ML, giving an average desorption rate of 8.4x10$^{-6}$ ML s$^{-1}$. 
Figure 2.2  (a) Arrhenius plots for the desorption of Cl, Br, and I from p-Si and for Br from lightly- and heavily-doped n-Si (labeled ldn- and hdn-Si), from which the kinetic parameters were determined. For Cl and Br, there are rate crossings at 700 - 800 K and the existence of a common point is possible within experimental uncertainty. For I, the observed rates are nearly three orders of magnitude larger than for Cl and Br. (b) Energy level picture for Si at 700 K. The Fermi levels are indicated by broken lines, and the energy zero is the valence band maximum (VBM). The double-headed arrows illustrate the activation energies deduced from experiment, (a). For Br, there is excellent agreement between the shifts in the Fermi levels and the relative changes in the activation energies. The activation energy for Cl desorption is greater than that for Br since the Si-Cl antibonding state lies further from the Fermi level due to the stronger Si-Cl bonding. The activation energy for I corresponds to the energy difference between the CBM and the Fermi level as the Si-I antibonding states overlap the CBM. Electron capture in the $\sigma^*$ states occurs for all samples, but a shift in the Fermi level changes the internal energy of the reaction.

Figure 2.3  A Meyer-Neldel plot showing that the parameters for Cl match well with those of Br, but that the I datum point does not fall on the line. The inverse of the slope, $\Delta_0$, is $66 \pm 5$ meV, and this characteristic energy indicates coupling to the optical phonons of Si.
3.1 Introduction

Cl₂ dissociatively chemisorbs to Si(100)-(2x1) [2]. At equilibrium, the resulting monatomic adsorbates terminate the dangling bonds (DBs) of Si dimers and step atoms [3]. As a result, the accepted Cl saturation coverage is 1 monolayer (ML), where 1 ML is defined to be the DB density \(6.48 \times 10^{14} \text{ cm}^{-2}\) of Si(100)-(2x1). However, first-principles local density functional calculations have predicted three stable, non-DB-terminated adsorption sites that may permit supersaturated Cl coverages in excess of 1 ML [4].

Figure 3.1 depicts the three non-DB-terminated adsorption sites for Cl adsorbates (LM1, LM2, and LM3), as determined by de Wijs, De Vita, and Selloni [4]. Cl adsorbates residing in LM1, LM2, or LM3 adsorption sites will be designated as inserted Cl adsorbates, Cl(i), to be distinguished from DB-terminated Cl adsorbates, Cl(a). LM1 is the lowest energy adsorption site for Cl(i), while LM2 and LM3 are both \(-0.2 \text{ eV}\) higher in energy than LM1 [5]. Electron stimulated desorption ion angular distribution (ESDIAD) experiments had previously established the presence of Cl(i) in LM2 sites upon Cl₂ adsorption at 100 K [6]. However, the LM2 ESDIAD signal intensity decreased

URL: http://link.aps.org/abstract/PRL/v98/e136104
upon warming to room temperature with a concomitant increase in the Cl(a) ESDIAD signal intensity [7].

In this chapter, I present a novel form of dissociative chemisorption for Cl$_2$ on Cl-Si(100)-(2x1) that generates kinetically trapped Cl(i), resulting in a Cl coverage ($\theta_{\text{Cl}}$) in excess of 1 ML. The supersaturated surface is shown to evolve along a previously unreported etching pathway that produces a surface characterized by dimer vacancy (DV) structures without the Si regrowth features associated with conventional halogen etching of Si(100)-(2x1) [8]. Scanning tunneling microscopy (STM) was used to study the etch rate dependence on time, Cl$_2$ flux, and temperature. Kinetic rate analysis was used to establish the insertion mechanism and test the validity of the proposed pathway.

### 3.2 Experiment

The experiments were performed in ultrahigh vacuum (base pressure 5 x 10$^{-11}$ Torr) using a room temperature Omicron STM and RHK electronics. The Si wafers were p-type, B-doped to 0.01-0.012 $\Omega$-cm, and oriented within 0.15$^\circ$ of (100). Preparation of clean and Cl-terminated Si(100)-(2x1) has been described elsewhere [9]. A solid-state electrochemical cell made from AgCl doped with 5 wt% CdCl$_2$ was utilized to generate a constant and controllable Cl$_2$ flux [10]. Supersaturation etching (SSE) was performed at 750 – 825 K with Cl$_2$ fluxes of 3 – 40 x 10$^{-3}$ ML/s. The extent of etching was determined by directly counting Si DVs in 4 – 10 STM images each spanning 100 x 100 nm$^2$, obtained on large A-type terraces far from steps. It is assumed that DVs neither diffuse nor annihilate at steps during SSE [11].
3.3 Results and discussion

The conventional Cl etching pathway, as determined by first-principals local density functional calculations [12], is depicted in Fig. 3.2. The etching process begins when a Si dimer with two Cl(a), 2SiCl, undergoes an isomerization reaction to form SiCl$_2$ + Si. To prevent the reverse isomerization reaction from occurring, the Si bystander can escape onto the terrace and become incorporated into Si regrowth features. The escape of the Si bystander increases the lifetime of the SiCl$_2$ unit and, in turn, the effective number of attempts to overcome the ~3.2 eV barrier to desorb [12].

The inset of Fig. 3.3 shows a Cl-saturated surface that has undergone conventional Cl etching at 800 K for 25 min. The surface is composed of dimer vacancy lines (DVLs) and etch pits, along with Si regrowth features. The main image of Fig. 3.3 shows a similarly prepared Cl-saturated surface that was held at 800 K while being exposed to a Cl$_2$ flux of 6 x $10^{-3}$ ML/s for 40 min. The surface is composed of DVLs “that have occasionally branched but, remarkably, there is no regrowth of the sort seen in the inset [1].”

Cl-free Si dimers are required for the Si bystander to escape and attach [12]. As such, the etch rate is expected to be zero on Cl-saturated surfaces, $\theta_{\text{Cl}} = 1$ ML. Indeed, investigations of the etch rate dependence on Cl coverage have revealed a maximum near 0.8 ML, with a sharp decrease toward zero as the $\theta_{\text{Cl}}$ approaches 1 ML [8, 13]. Thus, Cl-free sites must have been generated to account for the etching observed in the inset of Fig. 3.3. Trenhaile et al. demonstrated that the required Cl-free sites can be generated by phonon-activated, electron-stimulated desorption (PAESD) of atomic Cl [14, 15]. The resulting Cl-free sites pair to form bare dimers (BDs) and are easily observed in STM
images [15]. Examination of the surface in Fig. 3.3 reveals no BDs, implying that the Cl\textsubscript{2} flux replenished the Cl lost via PAESD and prevented the surface from undergoing the conventional etching reactions. Figure 3.3 also shows bright features (BFs) scattered about the surface that were not present on the starting Cl-saturated surface. On surfaces prepared such that BFs were present, together with Cl-free dimers, a mild anneal to ~700 K reduces the concentration of both. Therefore, BFs are associated with moieties related Cl(i). The lack of BDs and Si regrowth features in Fig. 3.3 further implicates the presence and involvement of Cl(i) in this novel etching mechanism, which I designate SSE.

SSE should involve steps associated with Cl\textsubscript{2} dissociation and Cl(i) adsorption, diffusion and pairing of Cl(i) to form volatile SiCl\textsubscript{2}, and finally desorption of SiCl\textsubscript{2}. To gain insight into the mechanism of Cl\textsubscript{2} dissociation and Cl(i) adsorption, images equivalent to that of Fig. 3.3 were obtained from samples exposed to Cl\textsubscript{2} fluxes of 3 – 18 x 10\textsuperscript{-3} ML/s during equivalent 800 K – 40 min cycles. The energy barrier to directly adsorb two Cl atoms from an impinging Cl\textsubscript{2} molecule onto a Cl-saturated surface was calculated to be 0.5 – 1 eV [4]. Thus, Cl\textsubscript{2} dissociation and Cl(i) adsorption is expected to be facile at 800 K and the concentration of Cl(i) should be directly proportional to the impinging Cl\textsubscript{2} flux. Furthermore, the etch rate would be expected to increase with flux since it is dependent upon the concentration of SiCl\textsubscript{2} that is derived from paired Cl(i).

From Ref. 1, Fig 3.4 “shows that the etch rate at 800 K initially increases with flux but then plateaus at ~ 6.51 x 10\textsuperscript{-6} ML/s. The same trend is observed at 825 K. The figure also shows a plateau region for 750 and 775 K. Thus, the etch rate has a distinct flux-independent regime at all temperatures studied. This is interesting as it implies that a simple picture of Cl\textsubscript{2} dissociation and insertion at saturated terrace dimer sites does not
apply – if it did, the insertion rate and hence the etch rate would increase monotonically with flux.

“The flux-independent regime indicates that insertion is mediated by special surface sites. We know that heating a Cl-saturated surface produces DBs by the PAESD process. These DBs should be able to induce Cl$_2$ dissociation [4, 16], thus potentially linking them to the insertion process. At a DB, the incoming Cl$_2$ molecule can dissociate with one Cl atom tying up the DB. The second atom can then either be scattered into the gas phase [16] or it can be adsorbed on the surface [4, 17] by inserting into a Si-Si dimer bond or back-bond.

“The flux-dependent regime of Fig. 3.4 reflects the fact that at lower flux values not all of the DBs created by PAESD see impinging Cl$_2$ molecules. These unreacted DBs are eliminated by capturing mobile Cl(i), which converts to Cl(a) [18, 19]. As the Cl$_2$ flux is increased, more DBs interact with impinging Cl$_2$ and the adsorption rate increases. This also reduces the conversion of the active etchant Cl(i) to Cl(a). The net result is an increase in the etch rate which continues until the flux is sufficiently high that all of the newly-created DBs react with the incoming Cl$_2$, representing the onset of the flux-independent regime.”

To better understand the presence of a flux-dependent and a flux-independent etching regime it is imperative to understand the Cl(i) adsorption process. Figure 3.5 shows the processes relevant to Cl(i) adsorption. Figure 3.5(a) depicts DB generation via PAESD, Fig. 3.5(b) depicts Cl$_2$ dissociation and Cl(i) adsorption, and Fig. 3.5(c) depicts Cl(i) decay to Cl(a). The relevant rate equations for each process are given below. From Refs. 14 and 15 the PAESD rate is
where $v_{PAESD} = 10^{10} \text{ s}^{-1}$ and $E_{PAESD} = 2.26 \text{ eV}$ are the prefactor and activation energy for PAESD, respectively. The rate of Cl$_2$ dissociation and Cl(i) adsorption, $R_{ads}$, can be written as

$$R_{ads} = sFN_{DB}$$

(3.2)

where $s$ is the sticking coefficient, $F$ is the Cl$_2$ flux, and $N_{DB}$ is the number of dangling bonds. The rate of Cl(i) decay can be written using terms from nucleation theory as the probability of a Cl(i) and DB encounter and is given as

$$R_{decay} = [\text{Cl(i)}]N_{DB}\sigma_{DB}k_{decay}$$

(3.3)

where $[\text{Cl(i)}]$ is the concentration of Cl(i), $\sigma_{DB}$ is the probability of Cl(i)-DB encounter, and $k_{decay}$ is the rate constant for decay. Under steady state conditions the change in $N_{DB}$ with respect to time is zero. Thus, from Fig. 3.5

$$\frac{dN_{DB}}{dt} = R_{PAESD} - R_{ads} - R_{decay} = 0$$

(3.4)

Combining Eqs. 3.1-3.4 and solving for $N_{DB}$ gives

$$N_{DB} = \frac{R_{PAESD}}{sF + [\text{Cl(i)}]\sigma_{DB}k_{decay}}$$

(3.5)

Substituting the expression for $N_{DB}$ from Eq. 3.5 into Eq. 3.2 ultimately leads to an expression for the rate of Cl(i) adsorption as a function of Cl$_2$ flux

$$R_{ads} = \frac{sFR_{PAESD}}{sF + [\text{Cl(i)}]\sigma_{DB}k_{decay}}$$

(3.5)

From Eq. 3.5 it can be readily seen that the rate of Cl(i) adsorption will initially increase with Cl$_2$ flux and approach the PAESD rate at sufficiently large fluxes. This trend is
directly reflected in the etch rate of Fig. 3.4 and distinguishes the rate of Cl(i) adsorption as the rate limiting step within the etching process.

To further substantiate the claim that Cl(i) adsorption is the rate limiting step, a reaction model, similar to that of Fig. 3.5, was constructed to depict the individual processes associated with SSE and is shown in Fig. 3.6. The model of Fig. 3.6 is assumed to describe SSE within the flux-independent etch regime so that \( R_{\text{ads}} = R_{\text{PAESD}} \) and the Cl(i) decay route is blocked. It is also assumed that BFs consist of 2 Cl(i) and are the precursors to SiCl\(_2\) formation, as will be discussed further in Chapter 4. A rate equation can be set up to describe the change in Cl(i) concentration with respect to time from Figs. 3.6 (a) and (b). Under steady state conditions this becomes

\[
\frac{d[\text{Cl}(i)]}{dt} = R_{\text{ads}} - 2R_{\text{BF}}^f + 2R_{\text{BF}}^r = 0 \tag{3.6}
\]

where \( R_{\text{BF}}^f \) and \( R_{\text{BF}}^r \) describe the rates of the forward and reverse BF formation rates, respectively. The factors of 2 reflect the fact that there are 2 Cl(i) per BF. A similar equation can be established for the change in BF concentration with respect to time from Figs. 3.6 (b) and (c)

\[
\frac{d[\text{BF}]}{dt} = R_{\text{BF}}^f - R_{\text{BF}}^r - R_{\text{SiCl}_2} = 0 \tag{3.7}
\]

where \( R_{\text{SiCl}_2} \) is the rate of SiCl\(_2\) formation. Combining Eqs. 3.6 and 3.7 gives

\[
R_{\text{ads}} = 2R_{\text{SiCl}_2} \tag{3.8}
\]

The SSE etch rate can be derived in terms of the SiCl\(_2\) formation rate by considering Figs. 3.6 (c) and (d). Under steady state conditions the change in 2SiCl\(_2\) concentration with time is zero, and therefore the rate of SiCl\(_2\) formation is equal to the rate of SiCl\(_2\)
desorption, which is simply the SSE etch rate. The result of this simple rate analysis is that the SSE etch rate is solely dependent upon the Cl(i) adsorption rate

\[ R_{\text{SSE}} = \frac{1}{2} R_{\text{ads}} \]  

(3.9)

It can then be concluded that the SSE etch rate is rate limited by the Cl(i) adsorption process.

From Ref. 1, “based on the above model, the Cl(i) adsorption process in the flux-independent regime should be rate-limited by the creation of DB sites. The insertion rate, \( R_I \), can be written as

\[ R_I = \sigma R_{\text{PAESD}} \]  

(3.10)

where \( R_{\text{PAESD}} \) is the rate of creation of DBs via PAESD and \( \sigma \) is the probability that atomic Cl produced from Cl\(_2\) dissociation leads to insertion [20]. Due to faster desorption rate, the total amount of Cl(i) is small and the Cl surface coverage is always near unity. From Eqs. 3.1, 3.9, and 3.10, the SSE etch rate can then be written as

\[ R_{\text{SSE}} = \frac{1}{2} R_I = \frac{1}{2} \left[ \sigma v_{\text{PAESD}} \right] \exp \left( \frac{-E_{\text{PAESD}}}{k_B T} \right) \]  

(3.11)

\[ \ln(R_{\text{SSE}}) = \ln \left[ \frac{1}{2} \sigma v_{\text{PAESD}} \right] - \left( \frac{E_{\text{PAESD}}}{k_B T} \right) \]  

(3.12)

“Fig. 3.7 shows an Arrhenius plot using the etch rates measured in the flux-independent regime of Fig. 3.3. From a straight-line fit to Eq. 3.12, we find that \( [1/2 \sigma v_{\text{PAESD}} ] = 1 \times 10^{9.0 \pm 0.2} \text{ s}^{-1} \) and \( E_{\text{PAESD}} = 2.27 \pm 0.04 \text{ eV} \). This value of \( E_{\text{PAESD}} \), obtained from SSE rate measurements, is in excellent agreement with that of \( 2.26 \pm 0.05 \text{ eV} \) determined directly from PAESD rate measurements on Cl-saturated Si(100). The PAESD experiments were done in the temperature range of 700 – 800 K following the
same protocol as Trenhaile et al. [15]. From these, we deduced a value of $1 \times 10^{10.0 \pm 0.3} \text{s}^{-1}$ for $\nu_{PAESD}$ [21] which gives a value for $\sigma$ of $0.2 \times 10^{0.4}$. Physically, this means that there is $\sim 1$ insertion event for every 5 Cl$_2$ dissociation events at DBs. The agreement between $E_{PAESD}$ and a physically meaningful value of $\sigma$ ($<1$) serve to confirm the insertion mechanism.

3.4 Conclusions

The observation of SSE, i.e. halogen etching without Si regrowth features, is a strong indication of the existence of Cl adsorbates in non-DB-terminated adsorption sites. It establishes the precedent that surface-related processes are not exclusively confined to the outer-most layers where DBs are typically located. Indeed, adsorbate-related processes occurring within sub-surface regions [22] must also be considered for a complete understanding of surface phenomena.

3.5 References


5. From Ref. 4, the adsorption energy of Cl$_2$ into two independent LM1 sites is $\sim 0.9$ eV.

7. From Ref. 4, the adsorption energy of Cl\textsubscript{2} resulting in 2 Cl adsorbates terminating DBs of the same dimer is ~5.4 eV.


20. For simplicity, the mild temperature dependence of $\sigma$ in the $750 - 825$ K range is neglected. Reference 13 found that the barrier for insertion via breaking the Si-Si dimer bond by a Cl atom is 0.5 eV. Thus $\sigma$ will increase by a factor of $\sim 2$ as compared to $\sim 24$ for PAESD from 750 to 825 K.

21. The attempt frequency for the PAESD process is rather low because it is a multi-phonon process, the details of which can be found in Refs. 14 and 15.

3.6 Figures

Figure 3.1 Calculated stable adsorption sites for Cl(i), as determined by Ref. 4. LM1 is located within the trough between dimer rows and Cl(i) is bonded to a 2\textsuperscript{nd} layer Si atom. LM2 is the bridge-bonded structure reported in Ref. 3. LM3 is located between the 1\textsuperscript{st} and 2\textsuperscript{nd} Si layer and Cl(i) forms a quasi-SiCl\textsubscript{2} unit with a Si atom of a surface dimer.
Figure 3.2 Conventional halogen etching pathway on halogen-terminated Si(100)-(2x1), as determined by Ref. 12. A fully halogen-terminated Si dimer undergoes an isomerization reaction to produce SiX$_2$ + Si. To prevent the decay of this newly formed species, the Si bystander escapes onto the terrace, creating a Si vacancy. The SiX$_2$ species ultimately desorbs and produces a Si dimer vacancy.
Figure 3.3  STM images of Si(100)-(2x1) acquired at room temperature. The dimer rows run from the lower left to the upper right. The inset shows the consequences of conventional etching/roughening for a Cl-saturated surface heated to 800 K for 25 min with dimer vacancy lines (DVLs), pits, and Si island regrowth features. (38 x 38 nm²; –3.0 V sample bias) The main image represents an equivalent surface that was heated to 800 K while being exposed to a Cl₂ flux of ~ 6x10⁻³ ML/s for 40 min. Etching has produced DVLs that have occasionally branched but there is no evidence of regrowth. Bright features like within the circle (BF) represents moieties related to inserted Cl (100 x 100 nm²; –1.4 V sample bias)
Figure 3.4  Etch rates for SSE in the range of 750 – 825 K as a function of incident Cl$_2$ flux. At 800 K, the etch rate initially increases with flux but then plateaus at \( \sim 6.51 \times 10^{-6} \) ML/s. The solid line is a guide for the eye. The same trend is observed for 825 K. For 750 and 775 K, the plateau region in etch rate is shown. Thus, the etch rate has a distinct flux-independent regime at all temperatures studied.
Figure 3.5  Individual processes associated with the Cl(i) adsorption process within the framework of SSE.  (a) Depiction of the PAESD process.  A single DB is generated from the spontaneous desorption of Cl(a).  (b) Depiction of Cl₂ dissociation and Cl(i) adsorption.  An impinging Cl₂ molecule interacts with a DB generated via PAESD resulting in termination of the DB and adsorption of Cl(i).  (c) Depiction of the decay of Cl(i) to Cl(a).  Cl(i) interacts with a DB generated via PAESD and decays to Cl(a), gaining a significant amount of energy.
Figure 3.6  Proposed processes involved in SSE within the flux-independent etch regime. (a) Depiction of the Cl(i) adsorption process. (b) Depiction of the BF formation process. Two Cl(i) diffuse about the surface and form a BF upon encounter. (c) Depiction of the SiCl₂ formation process. Upon surmounting an activation barrier the Cl(i)s associated with a BF pair on a single dimer to form 2 SiCl₂ units. (d) Depiction of the SiCl₂ desorption process.

Figure 3.7  Arrhenius plot using etch rates measured in the flux-independent regime of Fig. 3.4 giving the kinetic parameters for the SSE process. Straight line fit to Eq. 3.12 gives $1/2[\sigma v_{PAESD}] = 1 \times 10^{3.0 \pm 0.2}$ s⁻¹ and $E_{PAESD} = 2.27 \pm 0.04$ eV.
ATOMIC PROCESSES DURING Cl SUPERSATURATION ETCHING OF Si(100)-(2x1)³

4.1 Introduction

The structure and chemistry of Si(100) have been the subject of extensive experimental and theoretical studies. The importance of this surface resides in its use in the integrated circuit technology [1]. In particular, dry etching of silicon is an essential process that requires increasing precision due to the continual miniaturization of devices.

The clean Si(100) surface reconstructs, through dimerization, to remove one of the two dangling bonds (DB) associated with each atom on the bulk-terminated surface [2-4]. The remaining two dangling bonds, per dimer, control the chemistry of this surface. In principle, the dynamics of etching would seem to be simple, since there is only one desorption species, Si dihalide for Cl, Br, and I. However, extensive experimental and theoretical studies have revealed that even this apparently simple process presents a variety of complexities with subtle mechanisms involved. Structural insights into the etching by halogen atoms have come from studies using scanning tunneling microscopy (STM) that reveal the atomic scale morphologies [5-8]. In general, material removal from Si(100) by Cl and Br proceed via step retreat or layer-by-layer etching, resulting in bounded surface roughness [9-11].

Calculations on the interactions of halogens with Si(100) reveal the atomic-level events involved in surface reactions that lead to dihalide desorption [12, 13].

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studies of the dependence of etch rate on time, flux, and temperature have confirmed the reaction pathway for Si(100) proposed originally by Selloni and co-workers [14, 15]. Very recently, however, we found a new etching mechanism under conditions of supersaturation [16]. By exposing a saturated surface to a flux of Cl\textsubscript{2} at elevated temperature, we determined that etching is possible through a reaction pathway that leads to an unexpected final surface morphology. Here, we extend those studies and identify the structure of a previously mysterious surface moiety, the so-called bright feature (BF) observed during super-saturation etching (SSE) [16], allowing us to propose the sequence of events that control SSE and the energetics involved. Furthermore, we find that halogen dissociation at room temperature leads to insertion on a less than saturated surface and the resulting inserted species are kinetically limited from reaching an available dangling bond site.

4.2 Experiment

The experiments were performed in ultrahigh vacuum (base pressure 5 x 10^{-11} Torr) using a room temperature Omicron STM and RHK electronics. The Si wafers were p-type, B-doped to 0.01-0.012 \, \Omega \, \text{cm}, and oriented within 0.15° of (100). Clean Si(100)-(2x1) surfaces were prepared by standard thermal annealing procedures [17]. A solid-state electrochemical cell made from AgCl doped with 5 wt% CdCl\textsubscript{2} provided a constant Cl\textsubscript{2} flux that could be controlled through the applied voltage. After cleaning, the surface was exposed to Cl\textsubscript{2} while slightly above room temperature to reduce the concentration of water and related c-type defects [18]. The sample was then annealed at 700 K for 5 min to obtain a saturated Si(100)-(2x1) surface with very low defect density [19]. Super-
saturation etching (SSE) was achieved by exposing this surface to \( \text{Cl}_2 \) at 750 – 825 K. The flux was varied from 3 to \( 40 \times 10^{-3} \) ML/s, where 1 ML corresponds to the atom density of Si(100).

4.3 Results and discussion

The accepted reaction pathway for Si(100) etching proposed by de Wijs, De Vita, and Selloni is based on first principles local density functional calculations [12, 13]. Within a dimer, a monochloride-dichloride isomerization reaction generates a precursor \( \text{SiCl}_2 \) and a bare Si atom, the so-called Si bystander. The transfer of this Si atom to the terrace creates a vacancy adjacent to the \( \text{SiCl}_2 \), cutting off the reverse isomerization reaction and allowing the \( \text{SiCl}_2 \) unit to ultimately overcome the desorption barrier. In an alternative process, the \( \text{SiCl}_2 \) unit can transfer its Cl adatoms to neighboring Cl-free sites, if such sites exist, and that now-bare Si atom can also move to the terrace [20]. This gives rise to roughening without etching since there is no desorption. Both etching and roughening reactions produce Si dimer vacancies (DV) that can grow into dimer vacancy lines (DVL) and pits. In both cases, the transferred Si adatoms nucleate on the terrace to form regrowth islands. The STM image of Fig. 4.1(a) shows that heating a Cl-saturated surface at 800 K for 25 min produces pits and islands of different sizes that decorate the surface.

There is agreement that the etching/roughening reactions are hindered on halogen-saturated Si(100) [6, 7, 21] because Cl atoms on neighboring dimers preclude the escape of the Si bystander. However, Trenhaile et al. [22, 23] demonstrated that bare dimers (BD) can be generated on a saturated surface by phonon-activated electron-stimulated
desorption (PAESD) of atomic Cl. Once this occurs, the surface will etch/roughen through the conventional reactions, as shown in Fig. 4.1(a).

Until recently, it was believed that any etching would be not possible if the surface was exposed to a Cl₂ flux at high temperature to replenish the Cl lost via PAESD. Experiments showed, however, that etching does occur and this required a new reaction pathway [16]. Figure 4.1(b) shows a saturated surface after being heated to 800 K for 40 min while being exposed to a Cl₂ flux of 10⁻² ML/s. Despite the longer time at elevated temperature, compared to Fig. 4.1(a), the surface is less damaged as DVLs formed but without the concomitant regrowth islands. Significantly, the surface of Fig. 4.1(b) shows that there are no Cl-free dimers [24], implying that the Cl₂ flux was sufficient to replenish the Cl lost via PAESD and thereby preventing the conventional reactions. These findings led Agrawal *et al.* [16] to propose a new type of surface mechanism, termed super-saturation etching.

The etch pits observed on terraces exhibit size and shape distributions that reflect energy anisotropies around an existing pit [12]. Although energy differences are small compared to the desorption energy, they are sufficient to account for the patterns observed during etching. Once a single vacancy is created on a terrace, it destabilizes its neighbors and vacancy growth will tend to produce a linear vacancy. The fact that they are linear indicates that they are produced by vacancy extension since DVs and DVLs are nearly frozen on a saturated surface [25]. In the early stages of etching, as in Fig. 4.1(b), this gives rise to a dominance of linear pits that are one row wide. Steps are not expected to play a role in the observed pits as care was taken to acquire images on large A-type terraces far away from steps. Therefore, the diffusion and annihilation of existing DVs at
a step is frustrated during the super-saturation etching and the cooling down process since the Cl coverage is always $\geq 1$ ML.

Agrawal et al. studied the dependence of the SSE etch rate on flux in the range 750–825 K, finding that it became flux-independent for high enough Cl$_2$ fluxes. This implied that Cl$_2$ does not simply dissociate and insert at any terrace site, but that insertion was mediated by special surface sites, namely DBs that facilitate dissociation to produce an adsorbed Cl atom on the surface [13, 26, 27]. Before the flux-independent regime, the etch rate increased with the Cl$_2$ flux, indicating that not all of the DBs created by PAESD see impinging Cl$_2$ molecules. The etch rate increases until all of the DBs react with incoming Cl$_2$. Since Cl desorption creates the DBs, the PAESD rate should limit uptake and the subsequent etching reactions. When chemisorption takes place, one Cl atom ties up the DB and the second can be incorporated into the surface corresponding to uptake beyond 1 monolayer. These inserted Cl atoms, termed Cl(i), can diffuse to form SiCl$_2$ units that constitute the desorbing species.

In the flux-independent regime, the etch rate must be equal to the insertion rate and an Arrhenius plot measured in the flux-independent regime should be directly related to the PAESD rate. Agrawal et al. showed that the activation energy (2.27 eV) obtained from SSE rate measurements was in excellent agreement with that determined directly from PAESD rate measurements on Cl-saturated Si(100). They also showed that there was $\sim 1$ insertion event for every 10 Cl$_2$ dissociation events at DBs.

The SSE reaction path, as proposed by Agrawal et al., is portrayed in Fig. 4.2. The alternative pathway, including species $f$ was not proposed before and will be discussed below. SSE starts with a Si dimer with two terminally bonded Cl atoms, 2SiCl
(species $a$). Such species constitute most of the surface. The desorption of atomic Cl through PAESD generates Si$_2$Cl (species $b$). This species has a DB that facilitates the dissociation of an impinging Cl$_2$. When this happens, one Cl atom goes to the lowest energy adsorption site, the DB, while the second can be inserted into the surface, Cl(i), starred in the figure. We represent the inserted Cl as a dimer with three Cl atoms (species $c$), but we do not imply that this is the actual configuration since Cl(i) could insert at the valleys between dimer rows or in the Si backbonds, as discussed below. Cl(i) atoms can diffuse easily [13] and pair-up on a single dimer to form 2SiCl$_2$, labeled $e$, which is energetically more favorable than two units of $c$. If the impinging Cl$_2$ flux is not high enough, however, it is possible for Cl(i) atoms to find a dangling bond before encountering another Cl(i). This is described in Fig. 4.2 as a reaction that annihilates a Si$_2$Cl to form 2SiCl [28,29]. Desorption of one SiCl$_2$ unit produces species $g$, which has a single silicon atom. A DV is created with the desorption of the second SiCl$_2$ unit and, thus, there is no residual Si to produce regrowth chains or islands. DVs are nearly frozen on a Cl-saturated surface, implying that they do not diffuse to annihilate at steps during SSE [25]. Since etching is slightly more favorable near a DV than in a defect-free part of the surface, single DVs evolve into DVLs.

Within the described reaction path, two units of $c$ directly convert into one unit of $e$ upon their encounter. Although a viable pathway, it is incomplete in that it does not identify BF in Fig. 4.1(b). BFs are not present in conventional etching/roughening experiments, and are thought to be associated with moieties related to Cl(i). Selloni and co-workers determined three local minima (LM) binding sites for Cl(i) on a saturated surface [13]. In the one with the lowest energy, LM1, the Cl(i) resides in the valley
between two dimer rows bonded to a Si atom of the second layer. In LM2, Cl(i) can break a dimer bond to bridge two Si atoms. In LM3, a Si-Si backbond is broken and Cl(i) binds to a dimer Si atom. The Cl\textsubscript{2} adsorption energy for two Cl(i) in independent LM1 states is 0.9 eV; both LM2 and LM3 are 0.2 eV higher in energy than LM1. The diffusion of Cl(i) along the rows can take place on top of the dimers and through the valleys between dimer rows. When diffusing along a valley, a Cl(i) must move from an LM1 to the next LM1 and the activation energy is \(~0.3\) eV; while diffusing along a row, it must move from an LM2 to the next LM2 with an activation energy of \(~0.4\) eV. It is within reason to argue that due to the low diffusion barrier, species \(c\) is too mobile even at room temperature to be observed with STM. As such, BFs cannot be artifacts of a single Cl(i).

To confirm this, we prepared a surface that was \(~97\%\) saturated with 3\% of BDs and no BFs as shown in Fig. 4.3(a). We exposed this surface at room temperature to a flux of 4x10\textsuperscript{-3} ML/s of Cl\textsubscript{2} for 25 s, an amount of Cl\textsubscript{2} corresponding to 0.1 ML, to produce the surface shown in Fig. 4.3(b). From Fig. 4.3(b), the BD concentration decreased from 3\% to 0.67\%, and the surface had 0.24\% of BFs (referred to the surface dimer density). BDs can be distinguished from BFs because they are one dimer in width, in contrast to BFs that extend over 2-3 dimer rows. The surface was then annealed at 650 K for 5 min to facilitate the diffusion of Cl(i). Figure 4.3(c) shows that the BD concentration decreased from 0.67\% to 0.42\% and the BF concentration decreased from 0.24\% to 0.03\%. This indicates that BFs are related to a Cl-rich species that can provide Cl atoms for the available DBs. The changes in surface concentration were 0.25\% for BD and 0.21\% for BFs. Given the small densities and the variations in the densities on
the surface, we estimate an error in the difference in number of about 0.03%. To
determine these percentages, we analyzed several images of 50x50 nm$^2$ (~8500 dimers)
for each data point and from the dispersion in the number of features observed, we
estimated the error reported. We ran the experiment three times with similar results.
Since each BF saturates a BD, which has two dangling bonds, we conclude that each BF
must have two Cl(i) atoms associated with it. However, we cannot rule out that some
could have more than two Cl(i). Moreover, the fact that BFs are created at room
temperature suggests that Cl$_2$ dissociation and insertion has a very low barrier.

Species $e$ contains two Cl(i) and, if it corresponds to the observed BFs, an
Arrhenius plot of the BF density should give the difference in activation energies for Cl
insertion (or, similarly, Cl atom desorption) and etching. This can be derived as follows.
Since each Cl(i) leads to etching of one Si atom as SiCl$_2$, in the flux-independent regime,
the insertion rate must equal the etch rate. Also, the insertion rate is a fraction $\sigma$ of the
rate of creation of DBs via PAESD. Thus, $[BF]v_{et}\exp(-E_{et}/k_BT) = \sigma v_d\exp(-E_d/k_BT)$,
where $[BF]$ is the density of BFs, $v_{et}$ and $E_{et}$ are the prefactor and the activation energy
for the etch rate, and $v_d$ and $E_d$ are the prefactor and the activation energy for the Cl
desorption via PAESD. In the range of 750-825 K, Fig. 4.4 yields an activation energy of
0.2 eV. This means that the etching activation energy for species $e$ should be ~2.5 eV
(0.2 eV higher than that for insertion, which is 2.27 eV) if this species corresponds to the
BFs.

Selloni and co-workers determined two possible atomic configurations resulting
in two SiCl$_2$ units on a single dimer by breaking either the dimer-bond or a back-bond
and inserting Cl(i) [13]. The activation energy to desorb the first SiCl$_2$ was 1.4 eV or 1.9
eV, and the second was 2.9 eV for the dimer-bond breaking case. The bottleneck to create a dimer vacancy is clearly this second activation energy. Alternatively, Cl$_2$ from an incident flux could dissociate and saturate the DBs created by the first SiCl$_2$ desorption in the second layer before the second SiCl$_2$ desorption event. The second SiCl$_2$ desorption event then occurs at a cost of 2.5 eV.

In Ref. 13, we also learn that the adsorption energy of Cl$_2$ to produce any of the configurations with two Cl(i) atoms is 1.9 eV. A single unit of species $e$ is then 1 eV more favorable than two units of species $c$. For the described reaction scheme of Fig. 4.2, the energetics would be those shown in Fig. 4.5(a) reflecting that once species $c$ are formed, they diffuse to form species $e$ and gain 1 eV. To generate a dimer vacancy, once species $e$ is formed, a SiCl$_2$ unit would desorb readily even at 600 K (1.4 eV barrier). Due to its short lifetime, it is unlikely that configuration $e$ would be seen by STM, and we conclude that it is not the BF.

Species $g$ is much more stable than species $e$ (2.5 eV barrier to desorb as opposed to 1.4 eV). Though it might be tempting to associate $g$ with the BFs, there are two additional considerations that indicate this is not the case. First, the annealing experiments show that BFs can annihilate BDs so that BFs must have more than a single Cl(i). This is not compatible with configuration $g$ with a missing silicon atom and a single Cl(i). Second, BFs can be formed at room temperature, as was shown in Fig. 4.3. At room temperature, there is not enough energy to overcome the 1.4 eV barrier to desorb the first SiCl$_2$ unit from species $e$ to produce species $g$. Accordingly, we propose that the BFs constitute a precursor of species $e$ as depicted by $f$ in the alternative pathway of Fig. 4.2.
In the flux-independent regime, we are dealing with a series of reactions, one following the previous one. This means that species $c$ convert to $f$, $f$ convert to $e$, $e$ convert to $g$, and finally $g$ to DVs. The net reaction rates in any of these steps must be the same and constitute the etching rate. We must note that the reactions involving desorption are irreversible because reverse reactions to the conversion of $e$ into $g$ and $g$ into a DV are not possible.

Species $e$ converts very easily into $g$ by desorbing a SiCl$_2$ unit with an activation energy of 1.4 eV. This means that once formed, $e$ evolves very fast into $g$, leaving its concentration, $[e]$, very low. As such, the inverse reaction rate for the conversion of $e$ to $f$ is negligible and the etching rate is then given by the rate at which $f$ converts into $e$. By reinterpreting the results of Fig. 4 to account for species $f$, we find that this species is robust since its conversion to species $e$ costs ~ 2.5 eV, 0.2 eV higher than that for insertion, which is 2.27 eV.

4.4 Conclusions

In short, the proposed sequence of events taking place during SSE is the following. After insertion, the Cl(i)s diffuse and pair up to form species $f$, the BFs. In this picture, it is likely that two or more Cl(i) in close proximity attract each other to constitute a BF. BFs convert to species $e$ with an activation energy of 2.5 eV. Once species $e$ is formed, the first SiCl$_2$ unit desorbs easily, thereby cutting off the decay route back to species $f$. The final SiCl$_2$ unit desorbs at a cost of 2.5 eV, thus two SiCl$_2$ units desorb in irreversible reactions to create a DV.
These results also demonstrate that Cl insertion and BF formation are not restricted to the realm of SSE, i.e. elevated temperatures and saturated surfaces. Rather, insertion is dictated by the presence of DBs and coincides with dissociative chemisorption. Here, we showed that insertion occurred at room temperature and was mediated by the paired DBs of BDs on a less than saturated surface. However, at lower Cl coverages, the abundance of DBs facilitates the decay route shown in Fig. 2. The barriers for decay were calculated to be ~0.15 eV from LM1 and ~0.3 eV from LM2 [28]. At room temperature, these small barriers are easy enough to overcome on a nearly bare surface resulting in the Cl adsorption configurations described by Lyubinetsky et al. [30]. As a result, we only find evidence of Cl insertion as the Cl coverage nears 1 ML at room temperature and above from the presence of BFs. However, Cl insertion would account for the detection of a bridge-bonded Cl species, LM2, reported by Gao et al. after exposing Si(100) to Cl₂ at 100 K [31]. At such a low temperature it is quite reasonable that the decay route would be cut off, effectively freezing in the LM2 configuration despite the availability of nearby DBs. This interpretation indicates a very small barrier for insertion and exhibits the need for this process to be taken into account in the dissociative chemisorption of halogens.
4.5 References


52


Figure 4.1 STM images of Si(100)-(2x1) acquired at room temperature. The dimer rows run from the lower left to the upper right. (a) Conventional etching/roughening for a Cl-saturated surface heated to 800 K for 25 min with dimer vacancy lines (DVLs), pits, and Si island regrowth features. (90 x 55 nm²; –3.0 V sample bias). (b) Surface that was heated to 800 K while being exposed to a Cl₂ flux of ~6x10⁻³ ML/s for 40 min. Etching has produced DVLs that have occasionally branched but there is no evidence of regrowth. Bright features (BFs) that extend over three rows such as that within the circle, represent moieties related to inserted Cl (90 x 55 nm²; –1.4 V sample bias).
Figure 4.2  Species and mechanisms during SSE as proposed in Ref. 16 and in the present work. Large solid circles represent Si atoms, smaller circles depict Cl atoms, and Cl(i) are shown as stars. The oval in $b$ is a dangling bond. SSE starts with a chlorinated dimer, species $a$. Species $b$ is generated by Cl atom desorption. Thereafter, an impinging Cl$_2$ can dissociate at the dangling bond with one Cl atom attaching to the dangling bond and the second inserting into the surface as Cl(i), species $c$. As discussed in the text, insertion is depicted as a bridge bond, dashed lines in $c$ and $f$, but there are other local energy minima. For low Cl$_2$ flux, a Cl(i) atom can find a dangling bond before pairing with another Cl(i) atom. If this takes place, species $b$ and $c$ convert into species $a$. Cl(i) can diffuse and pair to form species $e$, as per Ref. 16, or, in an alternative pathway proposed here, form first species $f$ and then $e$. Species $e$ loses a SiCl$_2$ to form species $g$. The desorption of the second SiCl$_2$ unit generates a dimer vacancy without leaving residual Si for regrowth.
Figure 4.3 Image (a) represents a surface with ~97% Cl coverage with bare dimers (BDs) constituting ~3% of the total surface. Image (b) shows the surface after exposure to 0.1 ML Cl₂ flux at room temperature. The BD concentration decreased substantially and the surface displays many bright features (BFs). Image (c) shows the surface after annealing at 650 K for 5 min, demonstrating that the concentrations of both BDs and BFs decrease. These results indicate that each BF has two Cl(i) atoms associated.
Figure 4.4 Arrhenius plot of the bright feature density giving an activation energy of 0.2 eV.
Figure 4.5  Energetics during SSE as proposed in (a) Ref. 16 and (b) within the proposed reaction path in which species \( f \), corresponding to the bright features, has been included. In (a), Cl(i) species diffuse and form species \( e \), gaining 1 eV. Species \( e \) loses a SiCl\(_2\) unit by overcoming a barrier of 1.4 eV to form species \( g \). The second SiCl\(_2\) unit must overcome a barrier of 2.5 eV to generate a dimer vacancy without leaving residual Si for regrowth. In (b), inserted Cl atoms diffuse and pair up to form species \( f \). BFs need ~2.5 eV to evolve to species \( e \), which has two volatile SiCl\(_2\) units. Once species \( e \) is formed, the first SiCl\(_2\) unit can desorb with an activation energy of 1.4 eV. Species \( g \), which is more stable than species \( e \), produces a second volatile SiCl\(_2\) unit, with a cost of ~2.5 eV, and a dimer vacancy is formed.
CHAPTER 5

ADSORBATE-MEDIATED STEP TRANSFORMATIONS AND TERRACE REARRANGEMENT OF Si(100)-(2x1)

5.1 Introduction

Steps play a critical role in epitaxial growth and, for this reason, the step structure of Si(100)-(2x1) has been extensively studied [1]. Two distinct step structures result from the symmetry of the diamond lattice. Single height $S_A$ and double height $D_A$ steps are parallel to the dimer rows of the upper terrace while $S_B$ and $D_B$ steps are perpendicular to them. Early calculations by Chadi [2] predicted two configurations for $S_B$ and $D_B$ steps: rebonded and non-rebonded. Figures 5.1(a) and 5.1(b) depict the (non-rebonded) n-$S_B$ and (rebonded) r-$S_B$ structures. Despite the incorporation of a highly strained bond, the r-$S_B$ structure was predicted to be energetically favored, and scanning tunneling microscopy (STM) experiments showed that it dominates [3]. However, H-chemisorption alters the energy balance and the n-$S_B$ structure dominates [4, 5]. Recent studies have sought to address the mechanism by which the step transforms from r-$S_B$ to n-$S_B$ [6].

Theory has shown that dangling bonds (DBs) at non-rebonded steps are the least favored chemisorption sites for H [7], and chemisorption should occur there only after all other DB sites are saturated at a coverage of 1 monolayer. This has made studying step

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transformations difficult because it requires a controllable level of supersaturation to supply adsorbates to generate and saturate n-SB DB’s without inducing terrace etching. The recent discovery of a mechanism that leads to Cl insertion into Si-Si surface bonds allows for supersaturation [8], offering a way to control chemisorption at steps.

We use STM and density functional theory (DFT) to examine the evolution of the Si(100) step structure induced by Cl chemisorption at 700 and 725 K. We show that fine tuning of surface kinetic processes can direct inserted Cl atoms, Cl(i), from terraces to steps where they induce transformations on a manageable timescale. We identify a stable bridge-bonded adsorption site at the r-SB step that promotes accumulation of Cl(i) and initiates the transformation process through a sequence of events that includes r-atom etching and step retreat. Significantly, this is accompanied by unexpected changes in the lower terrace. These results can be generalized because H atoms, which had been predicted to reside in precursor chemisorption sites [9-11], can be the source of a similar restructuring process [12].

5.2 Experiment

The experiments were performed in ultra high vacuum (base pressure < 5x10^{-11} Torr) using an Omicron STM1 controlled by RHK SPM100 electronics. The Si wafers were p type, B doped to 0.01-0.02 Ω-cm, and oriented within 0.5° of (100). Clean surface preparation has been described elsewhere [13]. Once the surfaces were demonstrated to be contamination free, they were reheated and exposed to Cl₂ to achieve termination while still above room temperature, thereby minimizing water adsorption [13, 14]. Cl₂ was generated by an electrochemical cell of AgCl doped with 5 wt % CdCl₂,
giving a Cl$_2$ flux of 1.67x10$^{-3}$ ML·s$^{-1}$, where 1 ML = 6.78x10$^{14}$ cm$^{-2}$. Filled-state STM images were obtained at room temperature. The number of n-S$_B$ and n-D$_B$ step units and the extent of etching were determined by direct counting of 10-20 STM images, 50x50 nm$^2$ in area, per datum point. The DFT calculations used the generalized gradient approximation [15] with plane-wave-based ultrasoft pseudopotentials [16, 17] and an energy cutoff of 275.5 eV. The convergence criterion for geometry optimization was that all forces be less than 5.14x10$^{-2}$ eV/Å. Slab models of five Si layers were used for Cl-terminated Si(100) with the dangling bonds of the bottom Si layer terminated with hydrogen.

5.3 Results and discussion

Experiments have shown that exposure to atomic hydrogen below 625 K gives rise to n-S$_B$ steps [4, 12]. In contrast, there have been no reports of a similar change in step structure through Cl termination. The image in Fig. 5.1 shows the persistence of the r-S$_B$ structure after a saturation exposure of Cl$_2$ at 600 K. The bright dimer rows of the upper terrace terminate within the trough between dimer rows of the lower terrace. Rebonded Si atoms along the step have a circular appearance and can be easily distinguished from the oblong Si dimers. In Fig. 5.1, there is only one n-S$_B$ unit. Significantly, our calculations indicate that the Cl-terminated n-S$_B$ structure is favored by 1.8 eV/a over r-S$_B$, where $a = 3.84$ Å is the unit step length of Si(100). The rarity of the n-S$_B$ structure indicates an insufficient concentration of Cl at the step to activate the transformation.
To investigate step transformations, we reasoned that supersaturating the terrace might lead to Cl(i) accumulation at the step. Accordingly, we exposed a saturated surface like that of Fig. 5.1 to Cl$_2$ at 700 and 725 K. Under these conditions, single DBs are generated on the terrace by phonon-activated, electron-stimulated desorption of Cl atoms [18]. Once created, these now-active sites mediate the dissociative chemisorption of Cl$_2$ with one atom terminating the DB and the other inserting into a Si-Si bond with a probability of $\sim 10\%$ [8]. Whereas insertion is expected at room temperature, it is difficult to quantify because Cl(i) is highly mobile and readily converts into Cl(a), an adsorbed Cl atom, at a DB [19, 20]. Since the barrier for Cl(i) – Cl(a) decay is only $\sim 0.15$-$0.3$ eV [21], Cl(i) will decay before reaching the step. For saturated surfaces, this decay route is blocked.

Previous studies of Cl supersaturation above 750 K showed that Cl(i) atoms were lost when they paired on terrace dimers to form volatile SiCl$_2$ units [8]. The activation barriers for Cl(i) diffusion [22] and pairing [20] are 0.3-0.4 eV and 2.5 eV, respectively. The large barrier to pair hinders etching and results in an increase in Cl(i) concentration with decreasing temperature, as demonstrated by Aldao et al. [20].

By reducing the temperature to 700-725 K, we have found a regime where diffusion is facile but pairing and terrace desorption of SiCl$_2$ are minimal. Accordingly, mobile Cl(i) species can interrogate the surface and populate step sites. Instead of a relatively straight forward conversion of the step structure, however, we see that Cl(i) promotes etching of r-atoms and, ultimately, n-S$_B$ formation through the unexpected diffusion of vacancy lines across the saturated surface. This offers new insights into step
dynamics, while the diffusion of vacancy lines demonstrates that changes in the step structure can result in extensive restructuring of the lower terrace.

To establish an energetic correlation between Cl(i) accumulation and r-atom etching and n-S_{B} formation, we first determined a stable adsorption site for Cl(i) at the r-S_{B} step. Figure 5.2(a) depicts the initial Cl-terminated r-S_{B} step structure and Fig. 5.2(b) depicts that structure with Cl(i) forming a bridge-bond between an r-atom and an n-atom. The total energy of Fig. 5.2(b) is 0.34 eV lower than that of Fig. 5.2(a) [23]. Moreover, our calculations indicate that the step bridge-bonded Cl(i) is 0.5 eV lower in energy than terrace bound Cl(i) so that the site identified in Fig. 5.2(b) acts as a sink. Pairs of adjacent Cl(i)’s are bound with an energy of 0.4 eV.

Figures 5.2(c) and 5.2(d) depict a pathway whereby Cl(i) accumulation at bridge-bonded step sites creates a non-rebonded step. The structure of Fig. 5.2(c) was obtained by optimizing the geometry for two adjacent Cl(i) from two different initial conditions where both produced a bridge-bonded Cl(i) and a neighboring volatile SiCl_{2} with a DB at the step. SiCl_{2} desorption from both r-atom sites of a single step unit produces an atom-wide vacancy along an n-D_{B} step and gains 3.46 eV/a, assuming dimerization of the second layer Si atoms and Cl-termination of the resulting DBs, as shown in Fig. 5.2(d).

The STM image in Fig. 5.3 was acquired after 8 h of continuous Cl_{2} exposure at 700 K. Atom-wide vacancy lines (AVLs), like that shown, were commonly observed along or close to S_{B} steps at 700 and 725 K. In contrast, they were never observed above 750 K because the delicate balance between Cl(i) accumulation at steps and SiCl_{2} desorption from terrace sites was disturbed in favor of terrace etching. From the relationship between kink-length and step structure [24], we can conclude that the AVL
in Fig. 5.3 is derived from r-atom vacancies. The two-dimer-long kink separating step units 1 and 2 indicates that they should have the same structure. Unit 1 is r-SB and unit 2 should be as well. Similarly, units 3-8 and 10 should be r-SB, while units 9 and 11 should be n-SB. We conclude that the r-atoms expected below these units have been etched. The calculated STM image of the structure in Fig. 5.2(d), shown in the inset, is in excellent agreement with experiment.

From Fig. 5.2(d), r-atom etching initially produces an n-D_B step because of the vacancy line along the step. This can convert to n-SB if the vacancy line diffuses into the lower terrace while dimers shift toward the step. The anti-phase boundary (APB) in Fig. 3 provides evidence of vacancy line diffusion because an APB is produced when dimers shift in half-dimer-length increments [25]. In Fig. 3, the dimers below step units 6, 9, and 10 are out of registry with the lower terrace and the AVL is one dimer length away from these units. As a result, units 6 and 10 resemble pristine unit 11, which is n-SB. Unit 9 will be discussed below.

The rates of r-atom etching at 700 and 725 K were 1.48±0.13 x 10^{-4} and 0.94±0.10 x 10^{-4} \text{a}^{-1}\text{min}^{-1}, respectively, whereas the rates of non-rebonded step formation were 2.17±0.29 x 10^{-4} and 0.66±0.31 x 10^{-4} \text{a}^{-1}\text{min}^{-1}. These rates were calculated from the r-atom vacancy concentration and the number of non-rebonded step units (n-S_B and n-D_B) per step length after 1, 2, 4, 8, 12, and 16 hrs of Cl_2 exposure. Both display the inverse relationship with temperature seen for the concentration of Cl(i) [20]. Intriguingly, at 725 K the r-atom etch rate exceeds the non-rebonded step formation rate. Since etching produces non-rebonded steps, this suggests that some non-rebonded step units have reverted back to the rebonded structure despite the substantial energy
preference, 1.8 eV/\(a\), for the former. In particular, the vacancies below step unit 9 of Fig. 5.3 indicate that etching has occurred even though r-atoms can be seen along this step unit. In this case, the step unit must have retreated by a single dimer, through etching, and the n-SB structure has reverted back to r-SB.

Step retreat suggests a lower barrier for Cl(i) pairing on a step dimer than on a terrace dimer. De Wijs et al. [22] reported that the edge of a dimer vacancy accommodates Cl(i) and that the energy gained through 2SiCl\(_2\) formation at the ends of such a vacancy is 0.3 eV greater than if it were to form in a defect free region. They add that the desorption energy is \(~0\) for the first and ~1.0 eV for the second SiCl\(_2\) unit. By analogy, the S\(_B\) step should favor 2SiCl\(_2\) formation as there is more room for bond distortion and relaxation. Accordingly, n-S\(_B\) and n-D\(_B\) step dimers will be sinks for Cl(i) after the structure depicted in Fig. 5.2(b) is eliminated during r-atom etching. SiCl\(_2\) desorption from these sites will cause the step to retreat by a single dimer and regain the r-S\(_B\) structure.

Figure 5.4 provides evidence that the processes discussed above occur on a much larger scale than was expected. The STM image was obtained after 12 h of continuous exposure at 725 K. Surprisingly, it shows a terrace with two major domains labeled (2x1) and (2x1)', that are shifted relative to one another by a half-dimer unit, as evidenced by the APB. As in Fig. 5.3, the AVL is indicative of r-atom etching, while the APB can be associated with vacancy line diffusion away from the step. Since the step units bounded by the AVL all display the rebonded structure, each has retreated in a similar manner to unit 9 of Fig. 5.3, with further evidence given by the adjacent r-S\(_B\) units that are separated by a single-dimer-long kink across the APB.
Remarkably, the 16-dimer long kink identified in Fig. 5.4 signifies that etching and step retreat have occurred at each step unit along the (2x1)’ domain even though the AVL does not span the entire terrace below. We reason that the missing vacancy line segments have diffused across the terrace and annihilated at the S_A step. The AVL that can be seen is a remnant of this process and it has yet to annihilate at the step below. In this manner, the vacancy lines not only diffused ~7 nm away from the step, they also caused extensive terrace restructuring as the entire lower terrace shifted a half-dimer length (0.384 nm) toward the step in the wake of the diffusing vacancy lines. This implies a novel diffusion mechanism associated with vacancy lines, and it should rouse interest because conventional dimer vacancies cannot diffuse on Cl-saturated surfaces [26].

5.4 Conclusions

These results have counterparts in the H-Si(100) system, where definitive conclusions are elusive due to the numerous surface phases induced by H chemisorption. The n-S_B structure is produced at temperatures intermediate between those that produce (2x1) and (3x1) domains during H exposure, and it has been associated with the creation of dihydride chains at 520-610 K [12]. Below 520 K, dihydride chains cannot be distinguished from localized (3x1) and (1x1) phases, and their impact on step restructuring has been overlooked. However, their presence should be inferred from the kinks along the S_B step, as was the case for etching and step retreat in Fig. 4. In particular, both alter the relationship between kink-length and step structure. Moreover, the exposure conditions that lead to the n-S_B structure for H-Si(100) coincide with an
increased population of (secondary) adsorption sites beyond saturation [11], termed H(i) by analogy to Cl(i). These sites are similar to those predicted for Cl(i) [22], and they are predicted to decay and diffuse with barriers of ~0.2 eV [27] and ~0.5 eV [9], respectively. In contrast to Cl(i), H(i) should only be lost through H₂ desorption since SiH₂ does not readily desorb [28]. Our results, then, provide a unified picture of step stability by suggesting a similar formation mechanism for dihydride chains and n-S₆ steps on H-Si(100), namely, H(i) chemisorption and diffusion to the step, and dihydride chain formation and diffusion into the terrace.

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5.5 References


23. The energy contribution of full and half Cl$_2$ molecules and SiCl$_2$ units were used to ensure a consistent number of Cl and Si atoms throughout the calculations to allow for comparison.


Figure 5.1 Models of (a) n-S\textsubscript{B} and (b) r-S\textsubscript{B} steps identifying r-atoms and n-atoms, which form a strained bond in (b). The filled-state STM image (-2.00 V sample bias) shows an S\textsubscript{B} step after saturation with Cl at 600 K. The step is predominantly r-S\textsubscript{B}. R-atoms appear circular and are adjacent to steps, whereas dimers have an oblong appearance.
Figure 5.2 Calculated step structures relevant to r-atom etching. Periodic boundary conditions were applied to each calculation, so that the top and bottom rows of Si atoms, as presented, are equivalent. Only the top three Si layers are shown. (a) Initial r-S₈ step structure after Cl-termination. (b) Chemisorption of Cl(i) at the step forms a bridge-bond between an r- and n-atoms. It is \( \sim 0.5 \) eV lower in energy than for Cl(i) on the terrace. (c) Pairing of adjacent Cl(i)s produces volatile SiCl₂ units, gaining 0.4 eV relative to two isolated units. (d) Desorption of both r-atoms as SiCl₂ gains 3.46 eV/a, relative to (a), with dimerization and Cl termination of the exposed Si layer. The box is one unit of an r-atom vacancy line.
Figure 5.3  STM image (-2.00 V) of an S_B step after 8 h of Cl_2 exposure at 700 K. The AVL is composed of 18 r-atom vacancies. The units originating along step units 6, 9, and 10 have diffused to produce a continuous AVL and an APB where the dimers are out of registry with the lower terrace. Unit 9 has retreated by one dimer and regained the r-S_B structure despite undergoing r-atom etching. The inset is the calculated STM image (-2.00 V) of the structure depicted in Fig. 5.2(d).

Figure 5.4  STM image (-2.25 V) after 12 h of Cl_2 exposure at 725 K. The (2x1) and (2x1)’ domains reflect an extensive etching and terrace restructuring as each unit along the (2x1)’ domain has undergone r-atom etching and retreat. The resulting vacancy lines diffuse and annihilate at the S_A step. The AVL is a remnant that has yet to annihilate.
CHAPTER 6

COVERAGE-DEPENDENT CHEMISORPTION OF Cl ON Si(114)\textsuperscript{5}

6.1 Introduction

The single domain nature and long range ordering of structural components make high-index silicon surfaces attractive templates for self-directed growth applications [1]. Indeed, recent studies have revealed unidirectional growth of nanowires [2, 3] with high aspect ratios and tailored separation distances. Of the high-index surfaces, Si(114) is stable and planar residing 19.5° from (001) toward (111) [4]. It is structurally similar to vicinal Si(001) with alternating rebonded and non-rebonded double height S\textsubscript{5} steps [4, 5]. These steps produce three distinct structural units aligned along [\(\overline{1}00\)], as identified in Fig. 6.1. Their alignment suggests that Si(114) could also be used as a template for patterning via halogen-etching, though the structural consequences of such etching have not been investigated.

Here, we focus on the dissociative chemisorption of Cl\textsubscript{2} on Si(114) using atomic resolution scanning tunneling microscopy (STM) to develop the foundation for future investigations of etching. We identify the various adsorption site configurations through comparison of filled- and empty- state images and find preferred tetramer configurations.

\textsuperscript{5}Reprinted, in full, from \textit{Surface Science}, vol. 602, R.E. Butera, Abhishek Agrawal, and J.H. Weaver, “Coverage-Dependent Chemisorption of Cl on Si(114),” pp.475-480, Copyright (2008), with permission from Elsevier.
Sequential exposure and annealing cycles reveal that Cl adsorbs preferentially on rebonded atoms (R-atoms), then dimers, and finally tetramers with saturation at 1 monolayer (ML), where 1 ML is the dangling bond density of Si(114), 6.38 x 10^{14} \text{ cm}^{-2}. We show that $\pi$-bonding dictates the coverage dependence and controls the surface reactivity. These results provide a hint of the complexities that will be found upon etching at elevated temperatures, when Cl will redistribute itself as material is removed.

6.2 Experiment

The experiments were performed in an ultra high vacuum system having a preparation chamber for sample cleaning and Cl$_2$ exposure and an analysis chamber that housed an Omicron STM1 controlled with RHK SPM 100 electronics. The base pressure in each chamber was $< 5 \times 10^{-11}$ Torr. Samples were P-doped to 1-10 $\Omega$-cm, oriented within 0.5° of (114). Clean surfaces were obtained through heating at progressively higher temperatures for 1 minute intervals until reaching 1200 °C, while keeping the pressure below $10^{-10}$ Torr. A solid-state electrochemical cell [6] made of AgCl doped with 5 wt% CdCl$_2$ was used to generate Cl$_2$. The cell current was 2 $\mu$A, corresponding to a flux of $1.13 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$ on the sample. STM images were obtained at room temperature before and after exposure as well as after annealing at 550 K. Coverages were determined by direct counting after establishing the Cl signatures and are reported in ML. The Cl coverage on R-atoms ($\theta_R$), dimers ($\theta_D$), and tetramers ($\theta_T$) saturate at 0.25 ML, 0.25 ML, and 0.50 ML, respectively, in accordance with the dangling bond distribution.
6.3 Results and discussion

Figures 6.2(a) and 6.2(b) are representative images of the clean surface in filled- and empty-states, respectively. The insets identify the three surface structures. Density functional theory (DFT) calculations predict that each of these structures is buckled to some extent accounting for the corrugations in Fig. 6.2(a) [4, 7]. Buckling is most evident along the R-atom row where the “up” atoms appear as bright protrusions and the “down” atoms appear dark at this bias. The circle in Fig. 6.2(a) identifies a double R-atom vacancy where buckling is suppressed to the left and neighboring atoms of equivalent height can be seen. Figure 6.2(c) depicts the structural consequences of strain induced by rebonding of second layer silicon atoms. Our observations reveal that unbuckling occurs along both sides of an odd-length R-atom vacancy but only along one side of an even-length R-atom vacancy, consistent with Fig. 6.2(c).

Empty state images like Fig. 6.2(b) are dominated by bright, continuous rows that arise from R-atoms [4]; continuity is disrupted by vacancies like the one circled. The dimers have a similar appearance to those of Si(001), namely two features with a node in between [8]. The tetramers appear as two distinct features. One reflects the dimer bridge with a bright, bean-shaped appearance, and the other is associated with non-rebonded step atoms that appear as single atomic features.

Figure 6.3(a) shows that there is a marked reduction in the number of buckled R atoms after the adsorption of 0.16 ML of Cl. Terminating a dangling bond removes the buckling driving force, and the atoms relax to a symmetric configuration. The resulting redistribution of charge reduces the buckling of neighboring R-atoms within a decay
length of several atoms, leading to both Cl-terminated and Cl-free unbuckled R-atoms. The boxes in Figs. 6.3(a) and (b) contain both buckled and unbuckled R-atoms, as in Fig. 6.3(c). Figure 6.3(b) shows that the bright, unbuckled atoms at the right end of the box appear as a bright chain in empty states, as do the buckled atoms. The dark, unbuckled atoms at the center appear as four atomically-resolved features that are clearly distinguishable from the bright chain segments. The similar appearance of the buckled and the bright, unbuckled atoms in empty state images suggests that they are both Cl-free while the dark, unbuckled atoms are Cl-terminated. Cl adsorption is then similar to H adsorption on vicinal Si(001) where R-atom buckling was removed and the H-terminated sites appeared dark in filled state imaging [9].

Bright and dark dimers are also apparent after Cl adsorption. A dark dimer with Cl, DCl, is identified in Fig. 6.3(a). Previous investigations of Cl on Si(001) demonstrated that Cl-terminated dimers were dark in filled-state images because of a lower density of states near the Fermi level [10, 11]. The same should be true of dimers on Si(114) since they are structurally analogous. As discussed below, the concentration of dark dimers increases with exposure, as expected.

Chemisorption on the tetramers yields multiple configurations due to the four possible sites. As such, the tetramer rows appear more heterogeneous following Cl adsorption. Table 6.1 identifies five of the nine possible configurations, where Ia and IIa are circled in Figs. 6.3(a) and 6.3(b). Ia has a similar appearance to a bare tetramer except its right, non-rebonded step atom appears dark in Fig. 6.3(a) and bright in Fig. 6.3(b). Such a configuration is not observed on the clean surface. Since only a single site is altered in appearance, we conclude that Ia is singly-occupied as depicted in Fig. 6.3(d).
The right arm of IIa appears bright in comparison to the left in Fig. 6.3(a), and Fig. 6.3(b) shows that the dimer bridge images with a clear node in the center reflecting the breaking of the $\pi$-bond along the dimer bridge, Fig. 6.3(d). The remaining configurations are determined in a similar manner by comparing filled and empty state images, and their assignments agree well with their observed densities, as discussed below.

The total density of tetramers with at least a single adsorbed Cl is $1.95 \times 10^{13} \text{ cm}^{-2}$ and Table 6.1 gives the density of each chlorinated tetramer configuration. I$_a$ has a density of $1.47 \times 10^{13} \text{ cm}^{-2}$, accounting for roughly 75% of the total chlorinated tetramer population, while that of I$_b$ is negligible by comparison, $2.38 \times 10^{10} \text{ cm}^{-2}$. As shown in Table 6.1, both I$_a$ and I$_b$ have a single adatom but differ in the adsorption site with an overwhelming preference for I$_a$. Similarly there is a clear preference for configuration II$_a$ for doubly-occupied tetramers. More intriguing is the appreciable density of fully saturated tetramers, configuration IV, on this as-exposed surface.

These densities reflect the presence of $\pi$-bonds, as predicted in Ref. 7 and shown in Fig. 6.1, with a preference for those configurations that minimize the energy cost of broken bonds per Cl adatom. DFT calculations predicted that the tetramers have a $\pi$-bond along each arm, $\pi_{T_a}$, and a weaker $\pi$-bond across the bridge, $\pi_{T_b}$, where the relative strengths are a result of the difference in bond length (2.22 Å along the arm and 2.34 Å across the bridge [7]). I$_a$ breaks a single $\pi_{T_a}$-bond whereas I$_b$ breaks one $\pi_{T_a}$- and one $\pi_{T_b}$-bond. I$_a$ is then energetically favored and the enormous density discrepancy supports this conjecture. For the case of doubly-occupied tetramers, II$_a$ is the least costly, breaking $\pi_{T_a}$ and the weak $\pi_{T_b}$-bond. Though all of the $\pi$-bonds on a tetramer are
broken in IV, this configuration minimizes the total number of broken bonds per adatom along the row and, as such, should be the most stable.

The observed densities and preferences of Iₐ, IIₐ, and IV reflect the exothermicity of the chemisorption process. On Si(001), the adsorption energy for Cl₂ is ~ 5.4 eV [12], and we assume it is approximately the same on Si(114). This is more than sufficient to allow the products to interrogate the local potential energy landscape and find local energy minima. Due to kinetic limitations and the random impingement of the incident molecules, Iₐ is the most prevalent and the presumed initial tetramer adsorption configuration. The addition of a second adatom is then favored to produce IIₐ, requiring the disruption of the π₁ₐ-bond. The cost of a third adatom is one πₐ-bond, regardless of the site. However, the paucity of triply-occupied tetramers suggests that the unpaired dangling bond is very reactive and is almost immediately saturated, producing IV.

Kinetic limitations at room temperature prevent Cl from adopting the lowest energy chemisorption configuration for incomplete adlayers [10]. To drive the system toward equilibrium, we annealed at 550 K for 10 minutes. This low temperature precluded desorption, roughening, and etching reactions, but allowed diffusion. The image of Fig. 6.4(a) was obtained after exposure at ambient temperature and that of Fig. 6.4(b) after annealing. The total Cl coverage, θₐ, is ~ 0.095 ML in both images. In Fig. 6.4(b), the dimer and tetramer rows are more homogeneous and R-atom buckling has been significantly reduced. Figure 7.4(c) shows the increase in θₐ at the expense of both θₐ and θ₄. A similar observation was reported on vicinal Si(001) after annealing at 673 K [13]. In that case, the authors suggested that it might be due to a higher sticking
coefficient on R-atom sites or to thermally-activated diffusion from dimers to R-atoms. Figure 6.4(c) shows that it is diffusion on Si(114).

Cl-termination of an R-atom site is energetically favored since no \( \pi \)-bonds are broken. For Si(001), DFT calculations indicate an energy difference of \( \sim 0.30 \) eV for H-termination of two R-atom sites over a dimer site [14], in fair agreement with the dimer \( \pi \)-bond energy [12, 15, 16]. Here, adsorption prefers R, followed by dimer, and lastly tetramer sites in agreement with Fig. 6.4(c) and studies of the adsorption of ethylene [17].

Further exposure and annealing at 550 K produces the surfaces shown in Fig. 6.5 where \( \theta_{\text{Cl}} \) is \( \sim 0.34 \) ML in (a) and \( \sim 0.51 \) ML in (b). The Cl distributions are given in the insets. There is a significant increase in both Cl-terminated R-atom and dimer sites in Fig. 6.5(a), but the tetramer sites remain relatively Cl-free. \( \theta_{\text{D}} \) has reached 60% of its saturation coverage at 0.15 ML, even though \( \theta_{\text{R}} \) is only 72% saturated with 0.18 ML. In Fig. 6.5(b), \( \theta_{\text{T}} \) is no longer negligible at 0.08 ML although \( \theta_{\text{R}} \) and \( \theta_{\text{D}} \) at 0.22 ML and 0.21 ML are each shy of saturation. The population of less favorable sites reflects the fact that Cl must diffuse along \([\overline{0}01]\) with diffusion along \([22\overline{1}]\) becoming increasingly frustrated as \( \theta_{\text{R}} \) and \( \theta_{\text{D}} \) approach saturation. Accordingly, Cl will likely encounter another adatom along the dimer or tetramer row prior to encountering an unoccupied R-atom or dimer site, resulting in the pair-wise occupation of dimers and group-wise occupation of tetramers [10, 18, 19]. This is evident by the lack of single Cl occupied dimers in Fig. 6.5(a) and the presence of saturated tetramers (circle) in Fig. 6.5(b). Cl diffusion has an activation energy of \( \sim 1.1 \) eV along \([\overline{0}01]\) on Si(001) [20], and a similar activation energy is expected along the dimer rows of Si(114). Once grouped, however, diffusion is expected to occur in a pair-wise or group-wise manner [21], further inhibiting the
process. The result is dimer sites are populated as $\theta_{\text{Cl}}$ approaches 0.25 ML and tetramer sites as $\theta_{\text{Cl}}$ approaches 0.50 ML. The Cl coverage ultimately saturates at $\sim 1$ ML, producing a well-ordered surface with no sign of etching after annealing at 550 K.

6.4 Conclusions

We have shown that Cl site occupation on Si(114) depends on coverage and, after a mild anneal, adatoms bond to R-atom and dimer sites at $\theta_{\text{Cl}} < 0.50$ ML leaving the tetramer sites relatively Cl-free. These findings lay the foundation for investigations of the structural consequences of halogen etching, where the coverage dependence should have a profound impact [12, 22]. As etching occurs and material is removed, Cl will redistribute itself, leading to selective material removal and potentially novel pattern formations.

6.5 References


6.6 Tables

<table>
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<tr>
<th>Configuration</th>
<th>Density (cm⁻²)</th>
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<th>Broken bonds per adatom</th>
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<td>Others (combined)</td>
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<td></td>
</tr>
</tbody>
</table>

Table 6.1 Chlorinated tetramer configurations, densities and corresponding broken bonds per adatom.
Figure 6.1  Top and side views of Si(114). Rebonded step atoms (R), dimers (D), and tetramers (T) are identified and their alignment along $\overline{1}00$ is evident from the top view. The dashed lines represent the $\pi$-bonds predicted in Ref. 7. The solid line in the side view outlines a rebonded and non-rebonded double-height $S_8$ step, with respect to Si(001).
Figure 6.2  (a) Filled (-1.4 V) and (b) empty (+0.9 V) state STM images of clean Si(114). R-atoms, dimers, and tetramers are identified in the insets. Buckling of the R-atoms is apparent in (a) and depicted in the inset by a variation in size. A double R-atom vacancy is identified by the circle in (a) and (b). (c) Side view models of an R-atom row with a single-length (top) and double-length (bottom) R-atom vacancy to show how second layer rebonding affects buckling. The induced bond strain pulls adjacent R-atoms toward the vacancy, reducing buckling on both sides of a single-length vacancy but only on one side of a double-length vacancy.
Figure 6.3 (a) and (b) are filled (-1.6 V) and empty (+1.6V) images following exposure to Cl$_2$. In (a), adsorption reduces the amount of R-atom buckling relative to the clean surface and produces a contrast of bright and dark species. The rectangles highlight an R-atom segment depicted in (c) containing ‘up’ and ‘down’ buckled, Cl-terminated, and unbuckled R-atom sites. The arrow marked D$_{\text{Cl}}$ identifies a dark dimer that is Cl-terminated. Circles I$_a$ and II$_a$ call attention to configurations that are depicted in (d) where the gray sites are terminated with Cl.
Figure 6.4  Filled state images showing (a) the as-exposed surface and (b) the same surface after annealing for 10 minutes at 550 K. $\theta_{\text{Cl}}$ is $\sim 0.095$ ML. The redistribution of Cl is shown in (c), and it is evident in the reduction in buckled R sites along with a more homogeneous appearance of dimer and tetramer rows.
Filled state images, obtained after Cl₂ exposure and annealing, with insets that show the Cl coverage on R, D, and T sites in ML. θ\textsubscript{Cl} is ~ 0.34 ML in (a) and ~ 0.50 ML in (b). The distributions show that as the most favored become saturated, the next most favored sites begin to be populated. In (a), dimer sites are populated despite available R sites, and tetramer sites are populated in (b) despite the availability of both R and dimer sites. The lack of singly-occupied dimers in (a) and the presence of saturated tetramers (circle) in (b) show that Cl pairs on dimers and groups on tetramers prior to encountering an open and more favored site, thereby frustrating diffusion.
CHAPTER 7

 ADSORBATE-INDUCED ROUGHENING OF Si(100) BY INTERACTIONS AT STEPS

7.1 Introduction

Surface restructuring and roughening induced by even simple adsorbates such as hydrogen, carbon, oxygen, or nitrogen have been well-documented for many surfaces [1, 2]. Such surface changes are crucial for catalysis and corrosion, and they affect phenomena such as dissociative chemisorption, diffusion, recombination, and desorption. Moreover, there has been a great deal of interest in the discovery, understanding, and control of self-assembled nanostructures [3].

Experimental observations notwithstanding, relatively few theoretical studies have focused on the basic mechanisms underlying surface modification induced by adsorption. Zhdanov and Kasemo simulated the effects of three basic interactions on roughening temperature [4]. As depicted with a one-dimensional scheme in Fig. 7.1, these include an adsorbate-adsorbate lateral interaction ($E_1$) and two types of interactions between the adsorbates and the substrate ($E_2$ and $E_3$). Adsorbate-adsorbate interactions, $E_1$, induce roughening to minimize repulsion between adjacent adsorbates. An adsorbate can also weaken substrate particle interactions among themselves. In terms of modeling, this is indistinguishable from a second neighbor repulsive interaction between adsorbates and substrate particles, $E_2$, as both reduce the surface energy when the underlying substrate

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particle has neighbors. Finally, an adsorbed particle can have a direct attractive lateral interaction with a substrate particle, $E_3$, favoring step formation and then roughening. The effects of these interactions on an isotropic substrate have been studied in Ref. 5. The Si(100) surface is ideal for tests of the effects of adsorbate-substrate interactions, both theoretically and experimentally, because of its simple (2x1) reconstruction. It is also one of the most well-studied surfaces and the surface energetics are well known [6]. The adsorption of halogens on Si(100) are known to lead to roughening at relatively low temperature [7, 8], though models of roughening in the submonolayer regime are still unable to account for the formation of large pits and islands seen in experiment [9].

In this paper, we focus on a surface interaction that had previously been ignored, namely preferential adsorption at rebonded atoms along SB steps. Using high resolution STM, we first determine the equilibrium distribution of Cl on the Si(100) surface, finding that adsorption favors occupancy of rebonded atoms. This can be interpreted as an attractive interaction, termed preferential step adsorption interaction (PSAI), that lowers the step formation energy. Monte Carlo (MC) simulations that include this attractive interaction succeed in reproducing the general trends in roughening and surface patterns observed in the low-coverage regime, while simulations that ignore it have failed [9].

7.2. Experiment

The experiments were performed in ultra high vacuum (base pressure < $5 \times 10^{-11}$ Torr) using an Omicron STM1 with RHK SPM100 electronics. The Si wafers were $p$ type, B doped to 0.01-0.02 $\Omega$-cm, and oriented within 0.5° of (100). Surface cleaning has been described elsewhere [10]. Starting surfaces had point defects that amounted to
~0.01-0.02 ML, primarily in the form of dimer vacancies. Once cleaned, the surfaces were flash-annealed and exposed to Cl₂ at 600 K to minimize water adsorption [10, 11]. Annealing at 650 K for 30 s produced the desired equilibrium Cl distribution. Gaseous Cl₂ was generated by an electrochemical cell of AgCl doped with 5 wt % CdCl₂. A Cl₂ flux of 1.67x10⁻³ MLs⁻¹ was used, where 1 ML = 6.78x10¹⁴ cm⁻², the dangling bond density of Si(100). Filled-state STM images were obtained at room temperature, and the Cl concentration was determined by directly counting adsorption sites [12].

MC simulations of Si(100) were carried out using a square lattice of 100x100 sites where the surface was modeled as a 2-dimensional array of columns of height hᵢ,ⱼ. A restricted solid-on-solid model was adopted so that overhangs were not allowed, and periodic boundary conditions were used to avoid edge effects. The top of each column represents a substrate particle that was taken to be either a bare dimer or a Cl-terminated dimer. The energy anisotropy of Si(100) was modeled by defining Eₓ and Eᵧ as the nearest-neighbor interaction perpendicular and parallel to the dimer row direction, and these values alternate between adjacent Si layers so that Eₓ(h) = Eᵧ(h⁻¹) and Eᵧ(h) = Eₓ(h⁻¹), where h denotes the Si layer at height h. We adopted substrate interactions of 0.24 eV and 0.05 eV along and across the dimer row direction, respectively, consistent with known step formation energies [6].

The equilibrium configuration was obtained using the standard method of Metropolis. Two sites i and j were selected at random from an initially flat surface with Cl randomly located. A virtual transfer of a substrate particle i to site j was considered and the energy of the configuration was calculated, and compared to the energy of the initial configuration. If the system gained energy, the exchange was carried out.
Otherwise, the exchange was performed with a probability \( \exp(-\Delta E/kT) \) where \( \Delta E \) was a loss of energy (\( \Delta E > 0 \)). Next, an adsorbate and a bare site were chosen at random, and the adsorbate was moved to the new site according to the same method as above. The system evolved with successive jumps of substrate particles and adsorbates until it approached the equilibrium configuration. We ensured that the system reached equilibrium by monitoring the evolution of surface roughening. The simulation was ended when the roughness maintained a value within ±2% for at least 200 MC times.

7.3. Results and discussion

Figure 7.2 is an STM image of Si(100) that had a Cl coverage of 0.23 ML after it was annealed at 700 K for 2 hrs to reach equilibrium. At this temperature, etching by SiCl\(_2\) desorption is negligible but roughening is significant [7]. Although single dimer-wide regrowth chains and vacancy lines can be found scattered about the surface, most have organized into relatively large regrowth islands (I) and vacancy pits (P).

Previous MC simulations have failed to reproduce the trend of large and wide features at lower coverage [12] under the currently-accepted steric-induced roughening model [9] where roughening is thought to minimize the repulsion of adjacent adsorbates. The energy gained by keeping the Cl adatoms in isolation offsets that incurred by the introduction of steps. Figure 7.3(a) shows the results of a MC simulation, that included such steric repulsions for the equilibrium configuration with a Cl coverage of 0.3 ML. The steric repulsion strengths reported by Boland and co-workers were used (61 meV along the dimers row direction and 26 meV across) [8]. Within this model, one would not expect much roughening to occur in the low coverage regime (<0.5 ML) because
there are sufficient bare dimers to avoid neighboring adsorbate-terminated dimers. From Fig. 7.3(a), the simulation produces a surface where there was limited roughening and what had occurred was due to adsorbate density fluctuations [9]. In contrast to the experimental observation of Fig. 7.2, the simulated island and pit features were typically 1-2 dimer rows in width. The disagreement with experiment suggests the existence of another interaction that plays a key role in roughening at low coverage.

Chen and Boland addressed roughening in the low coverage regime by postulating an attractive anti-correlated dimer interaction [13]. In this model, filled dimers would cluster to maximize the amount of adjacent bare buckled dimers. For H-Si(100), this interaction produced “patches” of hydrogen, because steric repulsions were negligible. In contrast, the much larger Cl atom is randomly distributed since the clustering interaction nearly compensates the steric repulsion. We tested the effect of this anti-correlation interaction by modeling the Cl distribution as random. The steric repulsion values used to generate Fig. 7.3(a) were compensated by the anti-correlated dimer interaction, and the result is shown in Fig. 7.3(b). Again, the extent of roughening and the island/pit sizes do not match experiment. We conclude that random Cl distribution consistent with anti-correlation does not substantially increase substrate roughening.

The tendency for adsorbates to cluster, and thus enhance roughening, can be explained by considering Fig. 7.1. The anti-correlated dimer interaction can be interpreted as an attraction, $E_s$, between two adjacent bare substrate particles. Disrupted $E_s$ interactions due to adsorbates are labeled with X’s. Two adjacent adsorbates will disrupt three $E_s$ interactions while two isolated adsorbates will disrupt four. According to this, adsorption should be favored at sites along steps, at the upper or lower edge, since
this will disrupt an even fewer number of substrate interactions. When such an interaction was included in MC simulations, we found such a tendency for adsorption at steps. However, experiment shows that Cl is nearly random on the terraces, with no preference for upper step edges. One might argue that Cl clustering is then a consequence of a direct attractive interaction between adjacent filled dimers, as suggested for H-Si(100) in Ref. 14. However, the random distribution of Cl on the terraces indicates that the net interaction between Cl-filled dimers is negligible. The fact that roughening occurs, as in Fig. 7.2, forces us to conclude that another surface interaction is present.

The key to this new interaction can be found in the Cl distribution at S_B steps, as depicted in Fig. 7.4(a). For clean and Cl-exposed Si(100), the step is rebonded, with rebonded atoms identified as (1) [15]. The STM image of Fig. 7.4(b) shows a random distribution of Cl on the terrace after Cl_2 exposure at 600 K, to give a coverage of 0.13 ± 0.01 ML, and annealing at 650 K for 30 s. Under these tunneling conditions, the Cl sites are darker than bare sites. Examination of the S_B step reveals Cl attachment to rebonded Si atoms at the base of the step, labeled (1). Hydrogen atoms show a similar tendency to attach at these sites [16, 17].

The equilibrium Cl occupancy of distinct surface sites is related to the difference in adsorption energies, namely,

\[
\exp \left( \frac{\Delta E}{k_B T} \right) = \frac{\theta_S (1 - \theta_T)}{\theta_T (1 - \theta_S)}
\]

(7.1)

where \(k_B\) is the Boltzmann constant, \(T\) is the temperature, and \(\theta_T\) and \(\theta_S\) are the Cl occupancies at terraces and steps, respectively. STM images of more than 200 rebonded step sites show that the probability these sites were occupied was 0.65 ± 0.07. Since the
probability that a terrace site was occupied was $0.13 \pm 0.01$, the adsorption energy difference was $0.14 \pm 0.02$ eV at 650 K. We also observed a different Cl coverage at the lower sites at $S_A$ steps than at terraces, site (2) in Fig. 7.4(a). This interaction, much weaker than that at $S_B$ steps, could have non-negligible implications on the details of the resulting morphologies. Nevertheless, we only included the influence of the observed preferential adsorption at rebonded step sites in this work to determine if it could produce the type of features observed in Fig. 7.2.

While oversimplifying, we checked the influence of adsorption at rebonded step sites to determine whether it could yield the features observed in Fig. 7.2. Preferential adsorption adjacent to a step acts like the attractive adsorbate-substrate interaction $E_3$ from Fig. 7.1, in which the energetics depend solely on the adsorption site occupancy. The results of incorporating PSAI at $S_B$ steps for a coverage of 0.3 ML are shown in Fig. 7.5. Comparison to Figs. 7.3(a) and 7.3(b) shows that this interaction produced dramatic changes in surface morphology as large pits and islands developed. As a measure of surface disruption, the equilibrium pit areas increased from 5.9 % and 6.8 % in Figs. 7.3(a) and 7.3(b), respectively, to 15.3 % in Fig. 7.5. While the roughness is greater than that determined experimentally, we conclude that PSAIs at steps provide the needed surface processes that previous models could not produce. Even at very low coverage when roughening is expected to be much reduced, PSAIs are still present.

7.4 Conclusions

While PSAIs generate the needed large islands and pits at low coverage, it is clear that adsorption energetics cannot be completely described by considering only first
neighbor interactions. Indeed, the STM images show Cl adsorption close to islands and pits with different probabilities for rebonded atoms within a pit or at the edge of an island. The longer range interactions that account for the Cl populations could have non-negligible implications on the details of roughening, and it is likely that strains related to the formation of dimer rows could also be important in the total island and pit energetics on Si(100) [16]. Such finer adjustments are beyond the scope of this paper, the focus of which has been the role of first nearest neighbor PSAIs that provide an important step toward understanding roughening.

7.5 References


Figure 7.1  Schematic of adsorbate related roughening interactions from Ref. 4. Squares represent substrate particles and circles represent adsorbates. Arrows denote the interactions. $E_1$ is a repulsive interaction between adsorbates. $E_2$ is a next-nearest-neighbor adsorbate-substrate interaction that weakens interactions between substrate particles (x’s denote weakened $E_s$ interactions). It is equivalent to a repulsive interaction between adsorbates and second neighbors of the substrate. The anti-correlated dimer interaction discussed in the text acts as an attractive interaction $E_s$ between adjacent bare substrate particles. $E_3$ is a direct nearest-neighbor adsorbate-substrate lateral interaction.
Figure 7.2  STM image of Si(100) with a Cl coverage of 0.23 ML after annealing at 700 K for 2 h (75 x 75 nm$^2$, -3.0 V sample bias). The dimer row direction of the main terrace runs from the upper left to the lower right. Regrowth islands (I) and vacancy pits (P) are generally more than several Si dimer rows in extent. The circle in the inset (6 x 6 nm$^2$) highlights a Cl-terminated dimer that is darker in appearance than bare dimers in filled-state images.
Figure 7.3 Monte Carlo outcomes of a 100 x 100 lattice with 0.3 ML of Cl after reaching equilibrium. Bright features are regrowth and dark features are pits. Simulation (a) included steric repulsions of 61 meV along and 26 meV across dimer rows. Simulation (b) included effects of an attractive anti-correlated dimer interaction by considering that the adsorbate distribution was random. Neither (a) nor (b) produced the large islands and pits observed experimentally.
Figure 7.4  (a) Sideview of Si(100) showing the $S_A$ and $S_B$ step structures. Atom (1) at the $S_B$ step has shifted to form a long bond that defines the step as being rebonded. (b) STM image of a mixed step that was dominated by rebonded $S_B$ character (12 nm x 12 nm, -1.2 V). The Cl coverage is 0.13 ML. The distribution of Cl-filled dimers is nearly random on the terrace but examination of the rebonded atom sites reveals that 65% are occupied and appear dark in the image. The chemisorption energy difference between rebonded $S_B$ and terrace sites was found to be $0.14 \pm 0.02$ eV. Other sites, such as (2) which is close to an $S_A$ step, will have energy differences that are smaller.
Figure 7.5 Monte Carlo simulation (100 x 100 lattice with 0.3 ML Cl after reaching equilibrium) that included direct adsorbate-substrate lateral interactions of 0.14 eV at S_B steps. In contrast to Fig. 7.3, this produced large, extended regrowth features and vacancy pits. Comparison to experiment now shows good overall agreement.