Scanning Tunneling Microscopy Studies of Small Aromatic Molecules on Semiconductor Surfaces

by

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“Find beauty not only in the thing itself but in the pattern of the shadows, the light and dark which that thing provides.”

Junichiro Tanizaki
Abstract

Understanding the behaviour of molecules on a semiconductor surface is necessary if molecular self-assembly is going to be employed, with existing semiconductor technology, to create useful devices. Si(111)–7×7 is an invaluable surface upon which to study molecular adsorption. The surface reconstruction has been well characterized, and it possesses seven symmetrically distinct dangling bonds that can serve as reaction sites. Aromatic molecules on Si(111)–7×7 have been investigated with a variety of techniques and have been shown to chemisorb at room temperature. However, it is not trivial to predict how an ensemble of aromatic molecules might distribute themselves amongst the available bonding sites on this surface.

The work presented in this thesis begins with a joint STM and ab initio investigation of thiophene on 7×7 that demonstrates kinetics are necessary to describe the chemisorption sites occupied at various coverages. A kinetic Monte Carlo model, taking into account a mobile physisorbed state, is shown to accurately describe this site occupancy at room temperature. This model disregards molecule–molecule interaction because thiophene does not sterically hinder chemisorption to a neighbouring dangling bond. A larger molecule, mesitylene, was then studied on Si(111)–7×7, and shown to form an ordered molecular lattice on the Si(111)–7×7 surface. This is the
first demonstration of a porous molecular lattice grown on Si(111)–7×7 at room temperature. Finally, molecular chemisorption on the related 5×5 reconstruction, grown by depositing Ge on 7×7, is studied. It is found that the presence of Ge hinders molecular chemisorption, preventing formation of the mesitylene lattice.
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Statement of Originality

All STM data presented in this thesis were acquired by the author. All analyses of the STM data were performed by the author. The kinetic Monte Carlo model, described in Chapter 4, was written by the author.

The UHV system, described in Chapter 2, as well as the STM microscope head, BeetleI1, were designed by the author with the help and support of the nanoPhysics group. The cold stage was designed and constructed by Jason Visser. The sample puck and transfer arms, in their current state, were designed and constructed by Andrew Mark.

All ab initio calculations were performed by Roberto Miwa with the help of Gyaneshwar Srivastava. The author’s contribution was in providing unrelaxed atomic positions for the systems that included both molecules and surfaces.
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Chapter 1

Introduction

One of the goals of nanoscience is to control the properties of materials, devices and sensors at the nanoscale-level. The ability to arrange atomic and molecular adsorbates on a surface would open the door for a wide range of technological possibilities [1]. Organic molecules are of particular interest, not only because they can be selected or synthesized to have desired electrical or optical properties, but because they can be used as electronic devices [2]. Studying the adsorption and assembly of molecules on surfaces is appealing for two main reasons: the surface can act as a template for the adsorbate with specific reaction sites, and there exists a wide range of surface sensitive techniques to study the system. In particular, scanning probe techniques can image these systems with atomic resolution.

Semiconductors, such as Si or Ge, have directional bonds and the atomic positions of the surface reconstructions, discussed in Sec. 1.1, on their low-index faces are known. Understanding the factors that determine the binding sites of molecules on semiconductor surfaces could lead to methodologies for controlling the arrangement of organic molecules.
CHAPTER 1. INTRODUCTION

The Si(111)–7\times7 surface, one in a family of dimer-atom-stacking fault (DAS) surfaces [3], is an invaluable surface upon which to study molecular adsorption. The surface reconstruction has been well-characterized, and it possesses seven distinct unsaturated dangling bonds that can serve as reaction sites. In addition to structural differences, there are subtle electronic differences between these seven dangling bonds. Aromatic molecules on Si(111)–7\times7 have been investigated with a variety of techniques and have been shown to chemisorb at room temperature. However, it is not trivial to predict how an ensemble of aromatic molecules might distribute themselves amongst the available bonding sites on this surface. To date, no organic molecule has been showed to form an ordered molecular lattice on the 7\times7 surface at room temperature. Furthermore, there are no published reports of molecular adsorption on the related Ge/Si(111)–5\times5 surface.

This thesis presents STM studies of thiophene and mesitylene, two aromatic molecules, on semiconductor surfaces with DAS reconstructions.

Chapter 1 reviews DAS surface reconstructions, aromatic molecules and molecule–surface interactions, concluding with a review of previous studies of aromatic molecules on Si(111)–7\times7.

Chapter 2 outlines the experimental methods and materials, including the home-built UHV-STM system.

Chapter 3 describes the interaction of one thiophene molecule chemisorbed to a unit cell of Si(111)–7\times7. Both STM images and \textit{ab initio} results are discussed.

Chapter 4 describes the site occupancy of thiophene on Si(111)–7\times7. The results of a coverage-dependant STM survey are given and a kinetic Monte Carlo model,
based on activation energy barriers, is shown to describe the system at room temperature.

Chapter 5 presents the first data of mesitylene on Si(111)–7×7, showing the molecular lattice formed at high coverage.

Chapter 6 presents the first STM results of a Ge/Si(111) surface exposed to a molecular adsorbate and the passivating effect of Ge.

Chapter 7 includes some closing remarks and suggestions for further studies.

1.1 Si(111)–7×7

Atoms on the surface of a crystal are in a different environment from those in the bulk, and as such, the lowest-energy positions may not be the same as their positions in the bulk. When the Si crystal is cut along the (111) plane and annealed, the atoms find a new low-energy position. This new arrangement of atoms is called a surface reconstruction. In the case of Si(111), the basis vectors that describe the stable surface reconstruction have the same angle between them as the unreconstructed, or ideal, surface unit cell. The reconstruction can thus be described with Wood’s notation:

\[ m \times n \ R\theta. \]  

(1.1)

This surface reconstruction does not have the same periodicity as that of the bulk, but is \( m \times n \) times the size of the ideal surface unit cell and rotated by \( \theta \). When \( \theta = 0 \), the R term is omitted. In the case of Si(111), the stable reconstruction is 7×7.

Silicon is a tetravalent atom that has the diamond crystal structure. In the (111) direction, planes of Si atoms are repeated, to form what are commonly called bilayers. The top bilayer of the unreconstructed bulk crystal can be seen in Fig. 1.1 b), along
with the surface bilayer. The large unit cell of Si(111)–7×7, shown from the top in Fig. 1.1 a), does not consist of two symmetric halves. While the surface bilayer in the unfaulted half is aligned with the lower bilayer as it would be in the bulk, the faulted half is not. This incorrect registry is the stacking fault of the DAS reconstruction.

Pairs of atoms along the perimeter of the unit cell, marked in Fig. 1.1 a), as well as those that lie between the faulted and unfaulted halves of the unit cell, form covalent bonds with each other. These pairs are the dimers of the DAS reconstruction. The surface bilayer in each unit cell includes six atoms called rest atoms, shown in red, with unsaturated dangling bonds. The uppermost atoms, shown in blue in Fig. 1.1, are called the adatoms. By reconstructing to Si(111)–7×7, the number of dangling bonds drops from forty-nine to nineteen in each reconstructed unit cell: six that are localized above the rest atoms, twelve above the adatoms and one above the corner hole. Surface Si atoms, with three of the four valence electrons participating in chemical bonds, have one valence electron available that forms a dangling bond. While other DAS reconstructions have been observed, including the 5×5 reconstruction discussed in Sec. 1.1.1, 7×7 is the most famous of the dimer-adatom-stacking fault series of reconstructions [4, 5].

The surface bands of Si(111)–7×7 have been measured with angle-resolved photoemission and can be associated with the various dangling bonds using theoretical calculations. The adatom states dominate near the Fermi level, whereas the rest atom states are located near −0.8 eV [6]. It is the dangling bonds of the adatoms that are visible in STM images, shown in Fig. 1.2, due to the fact that they are closest atoms to the tip and that they have a high density of electronic states near the Fermi level1.

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1As explained in Sec. 2.1, the STM probes local electronic states close to the Fermi level.
Figure 1.1: a) A top and b) side view of the Si(111)–7×7 surface reconstruction, highlighting the dimers, the faulted half of the unit cell (stacking fault) and the adatoms. The dangling bonds are located above the adatoms, rest atoms and the corner hole atom.

The corner hole dangling bond is much more difficult to probe [7, 6]. The bands associated with the corner hole have been calculated to have a higher binding energy than the adatom band [8]. Thus, out of the nineteen electrons from the dangling bonds, the corner hole and rest atom dangling bonds are filled. This leaves five electrons remaining for the adatoms, giving an approximate filling of $\frac{5}{12}$ to each. These twelve adatoms are not identical but can be divided into six different types. On both the faulted and unfaulted halves, there are three adatoms in the corners of the triangular halves, and three on the edges. The corner adatoms have one nearest rest atom. The edge adatoms have two. In the literature, edge adatoms are also referred to as centre
Figure 1.2: a) Empty state (0.8 V, 0.5 nA) and b) filled state (-0.8 V, 0.5 nA) 20 nm × 20 nm STM images of a nominally clean Si(111)-7×7 surface show the dangling bonds of the adatoms. A unit cell is shown outlined in white. A faulted half unit cell (F) and unfaulted half unit cell (U) are marked. Images are not of the same area but are of the same surface.

or middle adatoms.

1.1.1 Ge/Si(111)-5×5

Closely related to the 7×7 surface is the 5×5 surface with only six adatoms. While Si(111)-5×5 can be grown by cleaving a Si crystal in vacuum and annealing, it is metastable and transforms to 7×7 for temperatures above 850°C. Germanium and Si both form the diamond crystal structure, but their lattice constants differ by approximately four percent (5.66 Å for Ge compared to 5.43 Å for Si) [9]. This lattice mismatch results in compressive strain that stabilizes the 5×5 reconstruction. This reconstruction is grown by depositing small amounts (<5 ML) of Ge on Si(111)-7×7 and annealing [10].

The DAS reconstructions discussed in this thesis are 5×5 and 7×7. For the studies
discussed herein, the corner hole atom is not a viable chemisorption site, and so the important atoms in terms of surface reactivity are the adatoms and rest atoms. The adatoms are the highest atoms and have dangling bonds with an average occupancy of \( \frac{5}{12} \) in \( 7 \times 7 \) and \( \frac{1}{2} \) in \( 5 \times 5 \). The rest atoms are on the surface bilayer and have filled dangling bonds, as mentioned above, because of charge transfer from the adatoms.

### 1.2 Aromatic Molecules

Within an organic molecule, a series of atoms with alternating single and double bonds that induces electron delocalization is called a conjugated system. This delocalization is easiest to understand by considering a chain of C atoms in which the p-orbitals of neighbouring atoms overlap. An aromatic molecule is a molecule with cyclic electron delocalization that provides enhanced thermodynamic stability. The archetypical example of aromatic molecules is benzene, \( C_6H_6 \).
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Figure 1.4: By extrapolating the observed energy difference in a) hydrogonating cyclohexene, an estimate can be made of the energy difference in b) hydrogonating 1,3-cyclohexadiene. This estimate corresponds well with the observed energy difference. It does not, however, correspond well for the case considered in c), the hydrogenation of benzene. [11]

To understand the thermodynamic stability, also called resonance stability, it is useful to consider the energy difference between products and reactants of a series of molecules closely related to benzene shown in Fig. 1.4 [11]. Each of the reactant molecules has one, two and three double bonds that are each to be saturated by a H$_2$ molecule. Saturation of the double bond in Fig. 1.4 a) experimentally produces a system -1.24 eV lower than the original reactants. From this, an estimate of the energy difference in Fig. 1.4 b) is $2 \times -1.24$ eV. Experimentally, it is observed to be -2.40 eV; this energy difference is very close. Estimating the energy difference for the reaction of benzene with three H$_2$ molecules produces a value of $3 \times -1.24$ eV = -3.72 eV. The observed energy difference is -2.16 eV. The discrepancy between these two values, -3.72 eV + 2.16 eV = -1.56 eV, is the resonance stability of benzene and is thought of as the energy required to break the delocalized electron ring.
CHAPTER 1. INTRODUCTION

Figure 1.5: a) Lewis diagrams, that represent electrons as localized, are inaccurate in portraying the electronic structure of benzene and so a resonance diagram or hybrid structure (right) is used. b) Aromatic five-membered heterocycles. c) Thiophene is shown in a ball and stick model as well, highlighting the α– and β–C’s.

Five-membered cyclic molecules can also have aromatic properties. Pyrrole, furan and thiophene are shown in Fig. 1.5. The C atoms closest to the heteroatom are called the α–C’s. Those further away are the two β–C’s. The heteroatom (N, O and S) is considered to donate two electrons to the aromatic ring, leaving a partial positive charge on the heteroatom. The contribution to the overall dipole from the resultant charge distribution of the electron donation is called the mesomeric dipole. However, all three heteroatoms are more electronegative\(^2\) than C. The effect on the overall dipole from the electronegative heteroatom is called the inductive dipole. The combination of inductive and mesomeric dipoles defines the resultant dipole of the molecule [12].

The delocalized electron ring makes reactions that require the molecule to be an electron acceptor (nucleophilic attacks) unlikely. Because of the electron transfer from the heteroatom to the electron ring, and thus the electron density of the HOMO is

\(^2\)Electronegativity defines the attraction of an atom to the electrons involved in covalent bonds with it.
low near the heteroatom, electrophilic attack rarely takes place on the heteroatom. Instead, the C atoms are the more likely candidates. Furan and thiophene, with a resultant dipole negative near the heteroatom, are more likely to undergo electrophilic attack at the \( \alpha \)-C’s.

### 1.3 Molecule–Surface Interactions

![Diagram of Molecule–Surface Interactions](image)

Figure 1.6: Molecules on a surface a) without a covalent bond between molecule and surface are physisorbed. Molecules can either b) chemisorb non-dissociatively or c) chemisorb dissociatively, in which case the various fragments can either chemisorb or desorb.

Molecule-surface interactions can be grouped into two broad categories: physisorption, as shown in Fig. 1.6 a), and chemisorption, as shown in Fig. 1.6 b) or c). A chemisorbed molecule has one or more covalent bonds with the surface, whereas a physisorbed molecules has none. This is the definition of a physisorbed molecule: a molecule held to the surface with no covalent bonds between the surface and the molecule. The force holding a physisorbed molecule to the surface is usually the van der Waal’s force. While a strict definition of van der Waal’s forces is any interaction excluding hydrogen bonding, covalent bonds and electrostatics, it is widely used as a synonym for the London dispersion force [13]. Temporal fluctuations in the electron density of a molecule induce a dipole that can either induce an image charge in a
nearby conducting material, or interact with another dipole. The London dispersive force is typically a weak force causing molecule–surface interaction strengths from 0.05 eV to 0.5 eV [14]. Physisorption has a few key characteristics, notably that the surface-molecule interaction is much weaker than chemisorption. The molecule deforms less and does not have to surmount an energy barrier between the initial state, in which molecule and surface are far from each other, and the final physisorbed state.

A chemisorbed molecule is bound to the surface through one or more covalent bonds, in which valence electrons are shared between atoms in the surface and in the molecule. Covalent bonds are characterized by a high electron density between atoms and usually have strengths from 1 to 10 eV [14]. As this process usually requires breaking of bonds internal to the molecule, or on the surface, or both, chemisorption usually requires the system to surmount an activation energy barrier before reaching the final state. A molecule that is close to the surface and likely to chemisorb it is said to be in a precursor state. This precursor state is often a physisorbed state, such as in the case of benzene [15, 16].

1.4 Small aromatic molecules on Si(111)–7×7

Benzene is the most studied aromatic molecule on Si(111)–7×7. It is a model system that acts as a useful guide for understanding the chemisorption of other aromatic molecules onto this surface. One of the first studies of benzene on Si(111)–7×7, in the mid 1980’s, incorrectly concluded that there was no stable chemisorption geometry [18, 19]. In 1991, two reports were published, each that clearly demonstrated, with temperature programmed desorption (TPD), that benzene both adsorbs and desorbs molecularly [20, 15]. That is, benzene does not desorb from the surface in fragments,
but instead as a complete molecule. The report by Taguchi and coworkers also investigated this system with electron energy loss spectroscopy (EELS) and concluded two important findings: at low temperature (≈90 K), benzene physisorsbs on the surface, and at room temperature, benzene is only present in a chemisorbed form [15]. Low temperature exposure of the surface to benzene produced spectra that were almost identical to gas-phase benzene data. After annealing to room temperature, the spectra changed drastically and Si-C stretching modes were observed while no Si-H modes were observed. Thermal desorption spectroscopy data showed desorption peaks that corresponded to a physisorbed state at 180 K and to a chemisorbed state at 320 K.

In 1995, the first STM results for benzene on Si(111)–7×7 were published by
Wolkow and Avouris [21]. While the dangling bonds of Si adatoms appear as protrusions in STM images, benzene exposure to the surface caused the adatoms to appear dark. By repeated measurements of the same surface area, they were able to conclude that benzene has a mean residence time of 2000 s and is equally likely to desorb or move to a new location on the surface. Because of the missing adatom in the STM images, they proposed that the delocalized electron ring bonds to the Si adatom dangling bond.

In a second STM experiment, conducted at 78 K, direct observation of the physisorbed, or mobile precursor, state was possible [17]. This state was notably different from the chemisorbed state because it appeared as a protrusion in the STM images. It also appeared to be strongly localized over the edge adatoms on the Si(111)–7×7 unit cell. Given that benzene requires the resonance stability to be broken before bonding, the chemisorption process is an activated process and the rate of chemisorption is described by

\[ k = A \exp \left( -\frac{E_a}{\beta} \right). \]  

(1.2)

This is a first-order Arrhenius equation, where \( A \) is an unknown prefactor with units \( s^{-1} \), \( E_a \) is the activation energy barrier height and \( \beta \), the thermal energy of the system, is \( 1/k_BT \). Assuming a prefactor of \( 10^{13} \text{s}^{-1} \), the authors were able to estimate the energies at each stage of the reaction between benzene and the Si(111)–7×7 surface, shown in Fig. 1.7\(^3\).

Fig. 1.7 is a representation of the lowest-energy pathway for the chemisorption of benzene, from the two being isolated systems to the final bonding geometry. Each of the local minima and maxima represents a stage in the chemisorption process:

\(^3\)If thermal energy, \( k_BT \), excites the system such that \( k_BT = \hbar \nu \), then a temperature of 295 K corresponds to a frequency of approximately \( 10^{13} \text{s}^{-1} \).
the isolated systems, the mobile precursor state, the transition state with which the activation energy barrier is associated, and the final binding state.

Figure 1.8: The chemisorbed spectrum of benzene was compared to that of a) 1,4 cyclohexadiene. b) Benzene bonds to an adatom-rest atom pair with opposite C atoms. This figure schematically illustrates the bonding; benzene does not align perpendicular to the surface in its chemisorbed geometry but lies almost flat on it.

The geometry of this final binding state was provided by a photoemission experiment published in 1998 by Carbone and coworkers [22], that involved comparing the spectrum of chemisorbed benzene to 1,4 cyclohexadiene, shown in Fig. 1.8 a). Two opposite C atoms each form a covalent bond to an adatom and nearest rest atom, as shown in Fig. 1.8 b). This bonding geometry has been verified with numerous other experimental and theoretical studies [23, 24, 25, 26].

1.4.1 Thiophene on Si(111)–7×7

Thiophene has been similarly investigated on Si(111)–7×7. Two of the earlier studies measured the thermal desorption and found that, like benzene, thiophene desorbs molecularly [27, 28]. Both of these studies reported desorption peaks around 350 K and 415 K. A further photoemission study of the C 1s peak showed two peaks in the C 1s core-level photoemission spectrum at 287.5 eV and 289.7 eV [29]. The authors claimed that each of these peaks was a unique binding mode of thiophene on Si(111)–7×7 and that the difference between α– and β–C’s was too small to resolve within
each peak. The two binding modes that were proposed involved interaction primarily with the S heteroatom and interaction primarily with the aromatic ring. Further experiments would show these hypotheses to be incorrect and, in the currently accepted interpretation, the two peaks are considered to be the $\alpha$– and $\beta$–C’s.

In 2000, a joint EELS and STM study revealed that thiophene chemically bonds to the Si(111)–7×7 surface via the $\alpha$–C’s [30]. STM images revealed the saturation coverage to be six molecules on each 7×7 unit cell. This implies that the saturation of the rest atoms prevents further chemisorption. EELS studies compared thiophene to $\alpha$–C-deuterated thiophene and showed a distinct chemical shift in the C-D bond, with no shift on the C-H bonds. A further study by the same group repeated the earlier thermal desorption experiment and observed only one peak [31]. An independent photoemission study of the Si 2p peak was also published in 2001 that confirmed the binding to an adatom–rest atom pair with the two $\alpha$–C’s by comparing the resulting spectra to 2,5-dihydrothiophene [32].

Finally, the adatom–rest atom binding mode was supported with a theoretical investigation of thiophene binding to an adatom–rest atom pair [24]. This investigation modelled thiophene chemisorption on a Si$_{16}$ cluster, terminated with 18 H atoms. The cluster simulated an adatom–rest atom pair. It concluded that there were two activation energy barriers in the chemisorption of thiophene, the first being 0.234 eV above the energy of the isolated components. The second barrier was reported to be at a height of 0.061 eV above that of the intermediate state. However, it also investigated benzene chemisorbing on the Si$_{16}$H$_{18}$ cluster, reporting that the first activation energy barrier is at least 0.399 eV above the energy of the isolated systems, in disagreement with results from [17]. While the prefactor used to calculate the $E_a = 0.30 \pm 0.03$ eV
term in [17] might be incorrect, the size of the cluster used to approximate the full 7×7 surface in [24] might be inadequate.

1.4.2 Furan and Pyrrole on Si(111)–7×7

Much less work has been done with either furan or pyrrole on the Si(111)–7×7 surface. Neither of these molecules exclusively forms covalent bonds with an adatom-rest atom pair. While furan can, it also forms dimers on the surface, in which each furan molecule has one α–C covalent bound to the surface and the other α–C bound to a neighbouring furan molecule [33]. Pyrrole, on the other hand, dissociates during chemisorption [34]. The N–H bond breaks and both the H atom and the remaining aromatic core, via the N heteroatom, bind to adatoms.

Outlook

Out of the four aromatic molecules presented in Fig. 1.5, only benzene and thiophene are known to chemisorb and desorb molecularly. They both have a known chemisorption geometry on the Si(111)–7×7 surface: to an adatom-rest atom pair. In contrast, four different chemisorption geometries have been observed for thiophene on Si(001)–2×1 [35]. Despite the fact that the surface unit cell of the 2×1 reconstruction is considerably simpler, comprising only a single Si dimer, thiophene can bond to the dimer in two different ways and also bridge two adjacent dimers in two different ways. Consequently, despite the fact that the unit cell of Si(111)–7×7 is considerably larger, the interaction of thiophene with the 7×7 surface is appreciably simpler.

The spatial and electronic inhomogeneity of the 7×7 reconstruction presents an
adsorbate with a variety of possible bonding sites on the centre or edge adatoms on either the faulted or unfaulted halves of each unit cell. STM allows the adatom involved in the chemisorption to be identified. For these reasons, thiophene is a good candidate for a combined STM and \textit{ab initio} study of chemisorption sites.
Chapter 2

Methods and Apparatus

The scanning tunneling microscope (STM) can be used to study the atomic and electronic structure of conducting surfaces and adsorbates [36]. To generate an STM image, a sharp conducting tip is brought close to the sample of interest. The interaction between tip and sample induces a tunneling current that can be used to control the height of the tip above the sample. Scanning the tip across the sample, line-by-line, allows a topographic map to be generated. Si(111)–7×7 was one of the first surfaces studied with STM [37], and the STM helped to determine the atomic positions in the surface reconstruction [4].

This chapter starts with an outline of STM theory and a description of the home-built microscope that was used to collected the images presented in this thesis. This microscope is housed in an ultra-high vacuum system, details of which are presented in Section 2.3. Finally, sample preparation and experimental details regarding molecular dosing and evaporator design are presented.
2.1 Theory of Tunneling Microscopy

Tunneling is a quantum mechanical phenomenon in which a particle passes through a classically forbidden barrier. A particle with energy \( E \), mass \( m \) and a wavefunction \( \Psi(z) \), in a potential \( U(z) \), can be described by the one-dimensional time-independent Schrödinger’s equation:

\[
E \Psi(z) = -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \Psi(z) + U(z) \Psi(z). \quad (2.1)
\]

With this description, the particle is no longer explicitly restricted to regions of space where \( E < U(x) \). This one-dimensional wave equation has exponentially decaying solutions for regions where \( E < U(x) \). In these classically forbidden regions,

\[
\Psi(z) = \Psi(0)e^{-\kappa z}, \quad \text{where} \quad \kappa = \frac{\sqrt{2m(U(z) - E)}}{\hbar}. \quad (2.2)
\]

Bringing a tip and a sample sufficiently close together causes a non-negligible overlap of the exponentially decaying wavefunctions. If there is a bias, \( V \), applied
between tip and sample, the respective Fermi levels will be offset by \( eV \) and a net current will be induced; more electrons will tunnel from states with higher occupancy to those with lower occupancy. The Fermi-Dirac distribution, \( f(E, T) \), describes the occupancy of the states as a function of energy, \( E \), and temperature, \( T \).

Assuming only elastic tunneling events, the resulting current can be estimated with the matrix element of the overlap of tip and sample wavefunctions, \( M(E) \). Let \( \rho(E) \) be the density of states at energy \( E \). The resulting current between the tip states, \( \rho_T(E) \), and sample states, \( \rho_S(E) \),

\[
I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} \left( f(E_F + eV + \epsilon, T) - f(E_F + \epsilon, T) \right) \times \left( \rho_T(E_F + eV + \epsilon)\rho_S(E_F + \epsilon) \right) |M(\epsilon)|^2 d\epsilon. \tag{2.3}
\]

In this equation, \( M \) represents the matrix elements between all tip and sample states at energy \( \epsilon \). If the temperature is low enough, the only states that will significantly contribute to tunneling will be those between the Fermi level and the applied bias \( V \). In other words, the Fermi distribution functions can be approximated by step functions and

\[
I = \frac{4\pi e}{\hbar} \int_0^{eV} (\rho_T(E_F + eV + \epsilon)\rho_S(E_F + \epsilon)) |M(\epsilon)|^2 d\epsilon. \tag{2.4}
\]

A method for calculating the matrix element, \( M_{\Psi\Phi}(\epsilon) \), between two decaying states, was provided by Bardeen [38] as an integral over a surface. In terms of STM, let \( \Psi \) describe the tip state at energy \( \epsilon \) and likewise \( \Phi \) describe the sample state at \( \epsilon \), both in isolation. The overlap is described by an integral over a surface \( S \), as indicated in Fig. 2.1, that lies between the tip and the sample:

\[
M_{\Psi\Phi}(\epsilon) = \frac{\hbar}{2m} \int \left( \Psi^* \vec{\nabla} \Phi - \Phi^* \vec{\nabla} \Psi(z) \right) dS. \tag{2.5}
\]
CHAPTER 2. METHODS AND APPARATUS

Spatial Resolution

The simplest approximation of an STM tip has all tip wavefunctions localized at a point \( \mathbf{r}_0 \). This case was considered by Tersoff and Hamann, as a precursor to considering a spherical tip \([39]\). In this case, assuming \( M(E) \) can be considered a constant over energy, the tunneling current

\[
I \propto \int_0^{eV} \rho_S(E_F + \epsilon, \mathbf{r}_0) d\epsilon.
\] (2.6)

That is, the tip probes the density of states of the surface at \( \mathbf{r}_0 \), between the Fermi level and the applied bias. Given that the atoms near \( \mathbf{r}_0 \) contribute strongest to \( \rho_S(E, \mathbf{r}_0) \), the STM is spatially a local probe.

Scanning tunneling microscopy is a technique that yields both electronic and structural information. The spatial resolution is dependent upon a tip having a highly localized apex wavefunction. The \( \rho_S \) term in Eqn. 2.4 describes the contribution of the density of electronic states of the sample. If the sample is biased, such that electrons tunnel from it to the tip, the resulting STM image is called a filled-state image. Reciprocally, if the data are generated by the electrons tunneling from tip to unfilled states of the sample, the image is called an empty-state image. A more detailed overview of the theory of STM is given in Ref. \([40]\) and references therein.

2.2 The Beetle

The head of the microscope performs two major functions: coarse approach, in which the tip is brought into tunneling range of the surface (approx. 2 Å) and scanning, in which the tip is rastered across the surface and its height (\( s \) in Fig. 2.1) is controlled. Most of the work presented in this thesis was taken with a homebuilt linear Besoke
beetle, similar to that previously used in our group [41, 42]. The key components are three piezoelectric ceramic (piezo) legs that support the chassis of the beetle, on which a scanner piezo is mounted. Fig. 2.2 shows the latest iteration, BeetleI1\textsuperscript{1} and the original design used in our group.

All motion of the beetle is accomplished via piezoelectric ceramics. Piezoelectric materials mechanically deform in response to an applied electric field. The ceramics used in the beetle design are all tubes with an inner electrode (grounded) and four quadrants of electrodes on the outside ($\pm X$ and $\pm Y$). In order to execute a coarse approach, where the beetle takes relatively large steps, the beetle uses a stick-slip mechanism, shown in Fig. 2.2 c) to e). The stick refers to slow application of opposite polarity voltages to opposite electrodes. This results in the tube bending but the ruby balls not moving on the surface. The slip is a quick return of the legs to zero, causing them to quickly straighten and the balls to slide along the surface.

In order to scan, the scanner piezo must raster the tip across the surface and vary height. The rastering is done in the same manner as the stick; application of opposite signals to opposite electrodes. Tip extension and retraction is performed by applying a signal to all quadrants. Each quadrant, therefore receives a voltage which is a sum of the rastering signal and the tip extension signal.

There were several issues BeetleI1 addressed. Connection to the high voltage wires was simplified with a set of body pins. The wings on the beetle, used for raising it during sample transfer, were brought lower to address one of the dominant vibration modes of the old design. Most importantly, the scanner piezo was replaced and a tip holder was designed to accommodate tip transfer.

\textsuperscript{1}BeetleI1 stands for Beetle Iteration One.
CHAPTER 2. METHODS AND APPARATUS

Figure 2.2: a) The current BeetleI1 used in these studies. b) The original Beetle for comparison. c) The beetle moves with slow application of opposite polarity voltage to either side of the leg piezos, causing them to deform as shown in d) (the deformation of the legs being exaggerated for illustrative purposes). When the bias is removed rapidly, e), the legs slide along the floor and the beetle takes a step.
2.3 The Chamber

Figure 2.3: A schematic of the UHV-STM system from the front (left) and top (right).

An ultra-high vacuum (UHV) environment is required for any study of the highly reactive Si(111)–7×7 surface. A detailed description of the need for UHV is given in App. A. All experiments are performed in a custom UHV system, shown in Fig. 2.3, with a base pressure of $5 \times 10^{-11}$ Torr. The preparation chamber (prep chamber) is directly attached to the ion pump and houses the titanium sublimation pump (TSP). The turbomolecular pump (turbo pump) is connected to the prep chamber via a six-inch valve.

The microscope is housed in the STM chamber, where the sample can be scanned or exposed to gas using the precision leak valve. When the sample is in the STM chamber, it is mounted in the cold stage. Transfer forks mounted on magnetic arms are used to move it to the prep chamber, where it can be cleaned and exposed to the flux from evaporators. There are two stages of vibrational damping: the sample rests upon a Viton stack in the STM chamber, shown in Fig. 2.4, and the entire UHV
system rests on an air table. Once in the cold stage, the cryostat tip can act as a heat sink via the Cu braid, and allows for temperature control down to 130 K.

![Cutaway view of the STM chamber](image)

Figure 2.4: Cutaway view of the STM chamber, showing the beetle above the sample, the Viton stack used for vibrational damping and the Cu braid used as a heat sink for low temperature experiments.

### 2.4 Sample preparation

#### 2.4.1 Preparing Si(111)–7×7

Si(111) wafers (Virginia Semiconductor, USA) were ordered precut to 5 mm × 15 mm. Initially, they are removed from their adhesive backing and cleaned by boiling in
methanol for approximately 10 min. One was mounted in the sample holder, ensuring firm and even contact on both sides. The sample holder is designed to allow a current to pass through the sample, allowing for resistive heating. It is held at a 6° angle to allow the STM tip to approach it with horizontal movement.

![Figure 2.5](image)

Figure 2.5: a) A silicon sample shown mounted in the puck, being held at 3.2 A (approx. 850° C). b) The sample and puck are shown on the heating fork. The transfer fork is used to move the puck into the STM chamber.

In the chamber, the sample is moved on forks, as shown in Fig. 2.5 b). The preparation chamber has a heating fork designed to interface with the current feedthrough on the sample holder. To clean the sample it is flashed to 1250°C for 40 s by passing 10.3 A RMS A.C. current through it. It is then held at 850°C (3.2 A RMS) to anneal it and lowered (1°C s⁻¹) to room temperature. The flash cycle is repeated until flash pressures are below 2×10⁻⁹ Torr.

### 2.4.2 Molecular deposition

All molecular adsorbates studied in this thesis were deposited from the gas phase. Thiophene and mesitylene (Sigma-Aldrich, USA) arrived in liquid phase at > 99% purity. A few millilitres were poured into a glass reservoir (MDC Vacuum, USA)
attached to the chamber as shown in Fig. 2.6. It was then purified by freeze-pump-thaw, requiring approximately seven cycles:

1. The reservoir was immersed in a liquid N\textsubscript{2} bath for approximately 5 minutes.
2. The reservoir valve was opened to the turbo pump for approximately 15 minutes.
3. The reservoir valve was closed and the liquid N\textsubscript{2} bath was removed.
4. Trapped gas will bubble from the liquid as it melts. If any bubbles were observed, steps 1–3 were repeated.

![Figure 2.6: Schematic of the gas handling apparatus.](image)

All exposures are measured in Langmuir (1 L = 1×10\textsuperscript{-6} Torr s) or milliLangmuir (mL), which is a measure of the pressure integrated over time. The ion gauge output (calibrated for N\textsubscript{2}) is recorded to calculate exposure. The observed coverage, however, depends on sample position as well. This implies that there is a pressure gradient specific to this chamber and, as such, the exposures are relative, not absolute. In
order to maintain uniformity, all exposures were conducted with the sample mounted in the STM chamber. When dosing with thiophene and mesitylene, the pressures required were so low that the turbo pump was unnecessary; the ion pump was able to bring the system back below $5 \times 10^{-10}$ Torr in minutes.

### 2.4.3 Ge deposition

![Diagram of Ge evaporator](image)

Germanium has a very low vapor pressure, and consequently it must be heated to high temperature to get it to evaporate. Electron-beam (e-beam) heating is an efficient manner to heat and sublime Ge. Electron-beam heating requires the material to be heated held at high voltage ($\approx 1$ keV), and an electron source, which is generally a hot filament. The electrons are accelerated through the potential difference and impact, in this case, Ge supported on W wire. The power of the evaporator can easily be measured by monitoring the current from the high voltage wire. Explicit details of this evaporator are given elsewhere [43], suffice to report it is a robust
evaporator that can be used to deposit Ge from the submonolayer regime to multiple monolayers.

Deposition was monitored with a combination of a quartz crystal monitor and the STM. The quartz crystal oscillates at a given frequency which changes in response to additional mass. The problem with a quartz crystal monitor is that it changes frequency as a function of temperature as well. It was used to calibrate the evaporator to a rate of approximately $1 \text{ Å min}^{-1}$ at which point the STM could be used for a more exact calibration of deposition. STM images can be used to count, atom-by-atom and molecule-by-molecule, the amount of adsorbate on the surface, assuming the stoichiometry of the observed structures is known.

2.5  \textit{Ab initio} Calculations

This section is meant as a brief description of the \textit{ab initio} method used for the calculations reported in this thesis. Details of the calculations are given in App. B, and a much more thorough description of theoretical modeling can be found in Ref. [44]. An \textit{ab initio} model uses the least number of approximations to describing a system. The systems described in this thesis, however, require the entire unit cell of Si(111)–$7\times7$ to be modeled, as well as the chemisorbed molecule, and it is not at present possible to solve the Schrödinger equation exactly for systems of this size, which require approximately 250 atoms. Two main approximations are required:

- Adiabatic approximation – A system can be considered as a collection of slow-moving ionic cores, modeled as pseudopotentials, and fast-moving valence electrons.
• Single-particle approximation – The many-electron wave function, in this case of the valence electrons, can be replaced by the density of electrons in the system. The density functional theory (DFT), pioneered by Hohenberg, Kohn and Sham, reduces the electron wave function to a set of single-particle equations that can be solved to determine the ground state of the system [45, 46]. In other words, each electron is independently considered within a potential that includes ionic cores, the external potential, and an exchange-correlation energy functional. The exchange-correlation energy functional is a correction term to incorporate electron-electron interactions. The simplest correction is the local density approximation, assuming at any given point the electron-electron interactions are equivalent to the interaction of an electron within a homogeneous electron gas. The results presented in this thesis use the generalized gradient approximation, which incorporates the derivative of the electron density at that point.

To simulate the ground state of a system, the SIESTA code was used [47]. This code models a system with periodic boundary conditions. For the simulations reported in this thesis, one unit cell of $7 \times 7$ with six layers of Si were modelled. The initial estimation of atomic positions, that is, ionic cores, is inputted. The program relaxes the system to the ground state by iteratively relaxing the electrons, after which the ionic cores are displaced relative to the force applied to each of them. The ionic cores are relaxed using Newtonian mechanics. The lowest-energy solution of each electron is a function of the density of electrons and thus relaxing the electrons requires looping through each electron multiple times until an applied convergence criterion is reached. Once the ionic cores have relaxed to a given convergence criterion, the system is in its ground state, and the structure and electronics are outputted.
Chapter 3

Thiophene on Si(111)–7×7

The first STM investigation of thiophene adsorbed onto the Si(111)–7×7 surface noted that at low coverage, thiophene does not distribute randomly over the available bonding sites but chemisorbs preferentially on edge adatoms in the faulted half of the unit cell [30]. This site preference has been observed for other simple aromatic molecules on the 7×7 surface, including benzene [21] and chlorobenzene [48]. The authors proposed that the electronic structure of Si(111)–7×7 made the faulted half of the unit cell more favourable for binding with thiophene [30].

The observed preference for thiophene to chemisorb to edge over corner adatoms, however, was explained in terms of steric strain. Strain has been previously proposed as an explanation for the site selectivity of aromatic molecules, in the case of chlorobenzene on Si(111)–7×7 [48]. In that paper, the authors state that the corner adatoms are under higher strain than the edge adatoms and thus are less favourable as chemisorption sites.

There is thus a predominant belief that the main difference between edge and corner sites is, in general, surface strain and that the main difference between unfaulted
and faulted halves of the unit cell is electronic in nature.

This chapter presents a new study of thiophene on Si(111)–7×7. STM images were taken at low coverages. These images revealed a previously unreported signature of thiophene chemisorption in filled state images. In order to explore the STM signature, and differences in chemisorption sites, all inequivalent binding geometries were modelled. These \textit{ab initio} calculations describe the structural and electronic changes after binding, as well as the total energy difference between isolated and bound systems. The structural deflections are used to calculate the surface strain energy.

### 3.1 STM Signature

#### 3.1.1 Procedure

Clean Si(111)–7×7 was prepared as described in Sec. 2.4.1. Thiophene was deposited using a precision leak valve as described in Sec. 2.4.2. During deposition, the difference between current pressure and the base pressure was monitored as a function of time. This allowed the exposure to be measured in milliLangmuir (mL). Normal exposures, as recorded by an ion gauge calibrated for N\textsubscript{2}, were approximately 50 mL. All data presented in this Chapter were taken at room temperature.
CHAPTER 3. THIOPHENE ON Si(111)–7×7

3.1.2 Observations

Figure 3.1: STM images showing the same area of Si(111)–7×7 with thiophene. Image details: 20 nm × 15 nm a) 0.66 V, 0.6 nA b) -0.6 V, 0.6 nA. c) Schematically, the area enclosed in a black rectangle shows a thiophene chemisorbed to an edge adatom.

An STM image taken of the Si(111)–7×7 surface showing thiophene molecules is presented in Fig. 3.1. In an STM image of a clean Si(111)–7×7 surface, such as the one shown in Fig. 1.2, the dangling bond of each adatom can be seen. The signature of thiophene adsorption, in both positive and negative biases, is a dark or missing adatom. The number of darkened sites increases with thiophene exposure.

When thiophene is exposed to the surface, it chemisorbs and forms covalent bonds with both an adatom and a neighbouring rest atom, as discussed in Sec. 1.4.1. The dark adatom is believed to be caused by a reduction in the density of states in the energy window that is accessible under these bias conditions by the saturation of
the adatom dangling bonds by surface–adsorbate bond formation. This behaviour is also observed for water [49], ammonia [50], acetylene [51], benzene [17, 21, 25] and chlorobenzene [48].

Figure 3.2: 12 nm×10 nm STM images at a) 0.66 V, 0.4 nA and b) -0.64 V, 0.4 nA showing corner and edge adatom adsorption sites. c) and d) are the same images with thiophene chemisorption features labelled.

Previously unreported are filled-state images of thiophene adsorption. This is more easily seen in Fig. 3.2. As well as a darkened, or missing, adatom, the two nearest adatoms, marked as Ad-B in Fig. 3.2 d), appear brighter. This behaviour has
been recently reported for benzene [26]. In their analysis, the authors claim that this observed response is due to charge transfer to the nearest adatoms.

The final attribute of thiophene chemisorption that appears in STM images is an adatom, marked as Ad-D in Fig. 3.2 d), not involved directly in the bonding, appearing dark. This adatom, labelled in Fig. 3.2 d), is in the neighbouring half unit cell. This is surprising, but shows that a result of chemisorption is observable across a dimer row.

3.2 Ab initio Results

3.2.1 Procedure

The purpose of the complementary ab initio calculations was to investigate each inequivalent binding site and the change in the surface after thiophene chemisorption. Initially, the ground–state configuration of an isolated thiophene molecule and the 7×7 surface, with no molecule, were calculated. The relaxed thiophene molecule was then positioned with its α–C’s above the adatom–rest atom pair at a distance previously determined by a cluster model of the 7×7 surface [24]. Finally, the combined system was relaxed.

There are six unique bonding geometries of thiophene on the 7×7 unit cell. In each half of the unit cell, thiophene can form a σ bond with either a corner or an edge adatom. While there is mirror symmetry on the bond between corner adatom and its nearest rest atom, the bond geometry involving the edge adatom does not possess that symmetry. In other words, thiophene bound to an edge adatom can have the S atom either closer or further from the centre of the half unit cell. Fig. 3.3 shows all
sites that were considered. Each calculation included the entire 7×7 unit cell.

Figure 3.3: Thiophene is simulated being bound to the 7×7 unit cell in the six unique bonding geometries.

### 3.2.2 Surface Deformation

The relaxed structure of Si(111)–7×7 with a thiophene molecule chemisorbed to it can be compared to the bare Si(111)–7×7 surface. At each binding site, thiophene adsorption caused an upward displacement of the adatom and a downward displacement of the rest atom. The trend was similar for both faulted and unfaulted binding sites and is reported, as per Fig. 3.4, in Table 3.2.2. The average adatom vertical displacement of all adatoms on the unit cell was 0.004 ± 0.002 Å. However, the two
closest adatoms to the rest atom that were not involved in the formation of new bonds, that correspond to those marked as Ad-B in Fig. 3.2 d), on average displaced upwards by 0.090 ± 0.010 Å.

Figure 3.4: After thiophene bonds to an adatom-rest atom pair, the adatom and the rest atom are displaced up and down respectively.

This surface deformation can be characterized in terms of the energy required to be in the new atomic positions. As a measure of this, the total energy of the Si(111)–7×7 unit cell, with adatoms in the positions they were after thiophene adsorption, was calculated. This gave a measure of strain energy, where

\[ E_s = E_{\text{SiDef}} - E_{\text{Si}}. \]  

(3.1)

\( E_{\text{SiDef}} \) refers to the total energy of the Si surface with the atoms in deflected positions. Values of \( E_s \) are reported for each bonding site in Table 3.2.2.
Table 3.1: Calculated atomic displacements and strain energies, $E_s$, of thiophene on Si(111)–7×7. Relative uncertainties are ±0.05 eV. All distances are given in Å. $Z_{12}$ is defined in Fig. 3.4.

<table>
<thead>
<tr>
<th>Site</th>
<th>Si Rest Atom</th>
<th>Si Adatom</th>
<th>$Z_{12}$</th>
<th>$E_s$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_C$</td>
<td>0.32</td>
<td>0.13</td>
<td>1.31</td>
<td>0.41</td>
</tr>
<tr>
<td>$F_{E1}$</td>
<td>0.32</td>
<td>0.13</td>
<td>1.31</td>
<td>0.45</td>
</tr>
<tr>
<td>$F_{E2}$</td>
<td>0.32</td>
<td>0.08</td>
<td>1.29</td>
<td>0.38</td>
</tr>
<tr>
<td>$U_C$</td>
<td>0.37</td>
<td>0.16</td>
<td>1.23</td>
<td>0.50</td>
</tr>
<tr>
<td>$U_{E1}$</td>
<td>0.37</td>
<td>0.16</td>
<td>1.23</td>
<td>0.52</td>
</tr>
<tr>
<td>$U_{E2}$</td>
<td>0.37</td>
<td>0.12</td>
<td>1.19</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 3.2: Calculated binding energies of thiophene on Si(111)–7×7. All values are ±0.1 eV. The adsorption geometries are defined in Fig 3.3.

<table>
<thead>
<tr>
<th>Site</th>
<th>$E^b$ (eV)</th>
<th>$E^b$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_C$</td>
<td>1.04</td>
<td>100.3</td>
</tr>
<tr>
<td>$F_{E1}$</td>
<td>1.04</td>
<td>100.3</td>
</tr>
<tr>
<td>$F_{E2}$</td>
<td>1.02</td>
<td>98.42</td>
</tr>
<tr>
<td>$U_C$</td>
<td>1.05</td>
<td>101.3</td>
</tr>
<tr>
<td>$U_{E1}$</td>
<td>1.03</td>
<td>99.38</td>
</tr>
<tr>
<td>$U_{E2}$</td>
<td>1.00</td>
<td>96.49</td>
</tr>
</tbody>
</table>

3.2.3 Binding Energies

A non dissociative reaction, such as this one, makes the calculation of binding energies relatively easy, as

$$E_b = E_{Si/tp} - E_{Si} - E_{tp} - \delta_{BSSE}. \quad (3.2)$$

Here $E_{Si/tp}$ is the energy of the Si(111)–7×7 unit cell with an adsorbed thiophene molecule, $E_{Si}$ is the energy of the isolated Si(111)–7×7 unit cell and $E_{tp}$ is the energy of the isolated thiophene molecule. The $\delta_{BSSE}$ term is required to appropriately correct for the fact that these calculations are done using local atomic orbitals as basis vectors, and upon addition of thiophene to the 7×7 surface, more atoms in the simulation
expand the number of basis vectors. It is explained in more detail in [52]. The binding energies for all sites are given in Table 3.2. This is perhaps the most interesting result: regardless of site, all binding energies are equal within error. This is consistent with the single maximum peak observed in TPD data [31], and compares well with the corresponding estimate of binding energy. Given a maximum desorption peak at 414 K [31], and using a prefactor of $10^{13}$ s$^{-1}$ as in Ref. [17], the binding energy can be estimated using Redhead’s method [53], as 1.14 eV.

3.2.4 Local Density of States

As expected from the STM data, the electronic bands of the Si adatom and rest atoms involved are suppressed near the Fermi level. This bandgap explains the dark or missing adatom that is the signature of thiophene adsorption. Fig. 3.5 b) and c) present integrated density of states images that are meant to simulate STM images. They are similar to the STM images in that a dark area is observed around the thiophene chemisorption site, and adatoms near the chemisorption site in the filled state image appear brighter.
Figure 3.5: a) The calculated projected density of states (PDOS) before (dotted) and after (solid) chemisorption for the four atoms directly involved in the formation of new covalent bonds, labelled in Fig. 3.4. b) and c) Integrating the local PDOS from $E_F$ to ±0.5 eV produces simulated STM images.

### 3.3 Analysis

Thiophene on Si(111)–7×7 was studied with STM and *ab initio* techniques. The generated PDOS images, shown in Fig. 3.5 b) and c), duplicate the observed darkened adatom at the chemisorption site. The low coverage STM images also display a previously unreported signature of chemisorption that included bright adatoms, labelled Ad-B in Fig. 3.2. The complementary *ab initio* calculations revealed that Ad-B
adatoms displace upward significantly after chemisorption. Currently, projected density of states plots, such as the ones shown in Fig. 3.5 a), are being generated by R.H. Miwa to further investigate the electronic difference with these adatoms after thiophene chemisorption. This will allow a complete understanding of the STM images.

The calculations also revealed that, upon binding to a thiophene molecule, the adatom displaces downward and the rest atom displaces upward. The total deformation of the surface, compared to the atomic positions in its isolated state, was used to calculate the strain energy. This calculation only weighed the structural deformation and neglected the electronic benefit of the thiophene molecule saturating two of the dangling bonds. From these it was found that all strain energies were noticeably lower on the faulted half of the unit cell. This is a surprising discovery as the main difference between faulted and unfaulted halves of the unit cell is generally described as electronic in nature [30]. This is, however, the first set of calculations that has modeled a di-σ bound adsorbate on all inequivalent positions on the Si(111)–7×7 unit cell.

Finally, the \textit{ab initio} calculations revealed the total energy difference between the sum of the isolated thiophene molecule and the bare Si(111)–7×7 surface, to the total energies of each of the chemisorbed geometries shown in Fig. 3.3. This was another surprising result: the binding energies of each is almost equal. One physical reason for this might be that while the strain required to bond to the faulted half of the unit cell is less, the energetic benefit of binding to the more electron-rich faulted half is less.
Outlook

The hypotheses put forward in [30] and [48] about strain and electronic benefits at the individual binding sites were proposed because STM data had shown a clear site preference for edge adatoms and the faulted half of the unit cell. The observation that there is a definite preference for certain adsorption sites in the Si(111)-7×7 unit cell, combined with the result that the binding energies at each site are almost equal, implies that site selection is determined by kinetics. This is consistent with the stability of the STM images that were acquired\(^1\). If thermodynamics were to play a large role, then the molecules would need to sample the available chemisorption sites. That there is an activation energy barrier to chemisorption is not surprising. While thiophene has not been directly observed in a precursor state on Si(111)-7×7, benzene has been with EELS [15], STM [17] and photoemission spectra [16]. The major result is that this site selectivity must be due to the kinetics of the reaction.

\(^1\)A STM investigation of chlorobenzene, another small aromatic molecule, noted that STM can observe only its chemisorbed state at room temperature, as the lifetime of the precursor state is approximately 100 ps [48]. Thiophene is expected to have a similar precursor lifetime.
Chapter 4

Thiophene Site Preference

One previous attempt to describe the site selectivity of adsorbates on the Si(111)–7×7 surface was the electronegativity and local softness analysis of Brommer et al. that involved modeling the entire unit cell without an adsorbate [8]. Local softness is the measure of a system at a point to accept or donate electrons while the external potential is being changed, and, when integrated in space around each adatom, can be used to derive rules for electrophilic and nucleophilic adsorbates on the 7×7 surface. The authors predict a reactivity pattern for electron donors that reproduces some aspects of thiophene chemisorption [8]. For example, they find edge sites in the faulted half cell to be preferred over edge sites in the unfaulted half cell. However, they also predict that for electron donors, the corner sites in the unfaulted half cell should be preferred over corner sites in the faulted half. Instead, thiophene prefers the corner sites in the faulted half cell. This suggests that a local reactivity index may not provide a complete description of thiophene adsorption. The molecule bridges a restatom/adatom pair and chemisorption is, therefore, intrinsically non-local.

In the previous chapter it was demonstrated, from the ab initio results, that this
observed preference is not a result of thermodynamics, but must be due to the kinetics of the reaction. The questions addressed in this chapter is whether differences in activation energy barriers can be used to describe the observed site selectivity. First, the possibility of using a set of closed-form expressions to describe the site selectivity is discussed. Then a kinetic Monte Carlo (kMC) model that was written to describe an ensemble of thiophene molecules adsorbing to the surface is described. The results of a thorough STM survey, used to describe site occupancy as a function of coverage, are presented. Finally, the results of the survey and the fit to the kMC model output are then discussed.

4.1 Failure of a Closed Form Description

Consider an initial population of thiophene molecules in a physisorbed state on the surface, $N_p(0)$. The Arrhenius equation describes the rate of overcoming an energy barrier $E$ as a function of temperature, $T$ and a prefactor $A$. Here $\beta = 1/k_B T$. It is a good starting point to describe the reaction rate, $k$, of thiophene from the physisorbed state to the chemisorbed state:

$$k = A e^{-E \beta}. \quad (4.1)$$

The reaction rate for an ensemble of molecules includes the number of available reactants and the number of available sites. If the rate at which, for example, the faulted edge adatoms are occupied can be written as $k_{ef}^e(t)$, then their occupancy

$$n_{ef}^e(t) = \int_0^t k_{ef}^e(\tau) d\tau. \quad (4.2)$$

One approach to describe $k_{ef}^e(t)$ would be as a product of $\kappa_{ef}^e$ and the available adatoms, rest atoms, and physisorbed molecules. In one unit cell, there are $3 - n_{ef}^e(t)$ unsaturated
faulted edge adatoms. Let $N_p(t)$ be the population of physisorbed molecules as a function of time.

$$k^e_f(t) = (3 - n^e_f(t))(3 - n^e_f(t) - n^c_f(t))N_p(t)\kappa^e_f.$$  \hspace{1cm} (4.3)

The $3 - n^e_f(t) - n^c_f(t)$ term represents the available rest atoms in that half unit cell.

While it appears Eqns. 4.2 and 4.3 can be used to generate coupled differential equations to describe the site occupancy, their fault is in accounting for remaining available sites after certain sites have been occupied. As an example, consider a unit cell in which a molecule adsorbs to an edge adatom. Two rest atoms, three corner adatoms and two edge adatoms then remain unsaturated. Each rest atom is surrounded by two edge adatoms and one corner adatom. As it has been saturated, the nearest corner adatom is now incapable of supporting a bond to a thiophene molecule. The unsaturated edge adatom as well has just lost one of the two available rest atoms beside it. One way of describing this cell would then be to say that there are now two available corner adatom sites and 1.5 available edge sites. While this suggests the available corner adatom sites can be rewritten $3 - n^c_f(t) - n^e_f(t)$, it is not universally correct, but rather depends on which site has been occupied.

The number of available sites is a function of the geometry of occupied sites that are in a half unit cell. The unique available configurations are shown in Figure 4.1. Depending on the sites that are occupied, there are various paths for further thiophene adsorption within that half unit cell. To correctly model adsorption upon the surface, each path must be available and this system of equations would not allow that.
Figure 4.1: a) A half unit cell with adatoms shown in blue and rest atoms in red. As thiophene saturates an adatom-rest atom pair, they are shown shaded in gray. b) The unique occupancy paths for a half unit cell with initially a corner chemisorption. c) The unique occupancy paths for a half unit cell with initially an edge chemisorption.
4.2 Kinetic Monte Carlo Model

In order to properly model the available surface bonding sites, a kinetic Monte Carlo model was written that incorporates both activation energy barriers for each site and a suitable description of the surface’s available dangling bonds. Thiophene molecules are initially placed over the surface, randomly, in a physisorbed state. At each timestep, they can move to a neighbouring half unit cell and can bond to an unsaturated adatom-rest atom pair. The probability of chemisorption to each of the unique adatoms, that is the faulted corner, $P_{cf}$, faulted edge, $P_{fe}$, unfaulted corner, $P_{cu}$, and unfaulted edge, $P_{eu}$, are the four model parameters that are used to fit the output of the model to the STM data. Coverage is determined by the number of molecules chemisorbed to the surface and so the model output, that is the occupancy of each of the unique chemisorption positions, can be plotted as a function of coverage.

The model surface is a set of unit cells that are divided into faulted and unfaulted halves, as shown in Fig. 4.2 a). Each half unit cell contains flags for three edge adatoms, three corner adatoms and three rest atoms. These flags are used to denote when a site has a molecule chemisorbed to it, and thus cannot be used for further chemisorption.

A certain number of molecules are placed in the physisorbed state above the half unit cells randomly, as shown in Fig. 4.2 b). At each timestep, each molecule has a chance of diffusion to a neighbouring half unit cell, desorbing, or chemisorbing. The probability of moving to a neighbouring half unit cell is a function of the number of chemisorbed molecules on that half unit cell. This was incorporated to reproduce the observation of benzene in a physisorbed state that did not indicate physisorbed molecules over chemisorbed sites [17]. Thus, the probability of movement to that unit
cell is decreased by one-third for each chemisorbed molecule on it. If a molecule is surrounded by half unit cells that are saturated, and it is above a half unit cell that is saturated, the molecule will desorb.

![Figure 4.2](image)

**Figure 4.2:** a) On the clean board, b) thiophene molecules are randomly placed. c) At each timestep, they can each move or chemisorb. d) Finally, the same counting can be done as with the STM images.

The molecule then has a probability of chemisorption to the half unit cell it is over. Assuming this is a faulted half unit cell, the two probabilities of interest are the probability of binding to a corner adatom, $P_c^f$, and the probability of binding to an edge adatom, $P_e^f$. The available sites are then enumerated in that half unit cell. A random number is generated that determines which site, if any, the molecule will chemisorb to. If it does chemisorb, the adatom and rest atom that correspond with that site are flagged and can no longer be used as reaction sites. The chemisorbed molecule can not desorb or move.
The modelled surface includes periodic boundary conditions. It was found that surfaces of $32 \times 32$ half unit cells converged with models including $64 \times 64$ half unit cells. At any given timestep, the number of molecules on each site can be counted. This output, site occupation as a function of total coverage, can then be compared to STM data.

4.3 STM Observations

4.3.1 Procedure

STM observations of the site preference were conducted at both room temperature, nominally 300 K, and at 130 K.
The 300 K experiments were conducted as in Sec. 3.1.1. Several experiments were conducted, with the surface being cleaned and then exposed to different amounts of thiophene to generate coverages up to almost saturation. The images from each experiment were then analyzed to determine occupancy as a function of coverage. On each half of the unit cell, the number of corner and edge adatoms that indicate thiophene chemisorption was counted. An image from a low-coverage experiment is shown in Fig. 4.3, with three of the faulted half unit cells enumerated.

At 300 K, contamination from the chamber was negligible and so the uncertainty in the measurements is statistical. In an experiment where \( M \) unit cells were counted, chemisorption sites were enumerated by the adatom that is saturated: faulted edge, faulted corner, unfaulted edge and unfaulted corner. If, for example, \( N_{f}^c \) faulted edge adatoms were counted as dark or missing, then the average occupancy of thiophene molecules on faulted edge adatoms per unit cell,

\[
    n_{f}^c = N_{f}^c / M.
\]  

The statistical uncertainty \( \delta N_{f}^c = \sqrt{N_{f}^c} \). Thus

\[
    \delta n_{f}^c = \sqrt{N_{f}^c} / M. \tag{4.5}
\]

The 130 K experiments were conducted in a similar manner. First the cold stage was allowed to cool to its base temperature. Then the sample was flashed and moved to the STM chamber, where it thermally equilibrated with the cold stage. Cooling took approximately thirty minutes, and while it was at cryogenic temperatures, it pumped more of the residual gas from the chamber than at room temperature.

On top of the statistical error, therefore, there was a non-negligible systematic error of false positives caused by adsorption of the residual gas. STM images taken
of the clean 7×7 surface at 130 K were used to calibrate this systematic error. From these images, the number of defects, $B_1$, was counted on $M_1$ unit cells. Assuming a normal error distribution, the error on $B_1$ was assumed to be $\sqrt{B_1}$. Once thiophene was deposited, the number of dark adatoms, $N_i$, was counted on $M_2$ unit cells for each of the four adatom types. The real number of thiophene sites on each unit cell, $n_i$, is the difference between the total number of dark spots observed and the defects. First the defect number was normalized for the observed number of unit cells and the number of adatoms (assuming the defects are randomly distributed among each of the four different observable adatom type):

$$B = B_1 \frac{M_2}{4M_1}$$

and

$$\delta B = \sqrt{B_1} \frac{M_2}{4M_1}$$

Finally the real number of thiophene sites per unit cell was given by

$$n_i = \frac{N_i - B}{M_2},$$

and

$$\delta n_i = \frac{\sqrt{N_i + B}}{M_2}.$$
4.3.2 300 K Observations

Figure 4.4: For each distinct adatom type identified in STM images, the average occupancy is shown as a function of total thiophene coverage per unit cell.

The average occupation of each of the four distinguishable sites as a function of thiophene coverage is shown in Fig. 4.4. This is the result of having counted over one thousand half unit cells.

The faulted and unfaulted halves do not share adatoms or rest atoms and can be considered distinctly. Fig. 4.5 shows a plot of the total occupancy of faulted and unfaulted halves, that is the sum of edge and corner occupancies, as a function of coverage. From these plots it can be seen that, at room temperature, the faulted half of the unit cell is preferentially occupied before the unfaulted.
CHAPTER 4. THIOPHENE SITE PREFERENCE

Figure 4.5: The preference for faulted over unfaulted halves of the unit cell and for edge over corner adatoms is clearer when averaging over the unit cell.

Fig. 4.5 also includes a plot of the average edge and corner occupancy as a function of coverage. From this plot it is clear that edge adatoms are preferred regardless of coverage. However, this plot is of the total average coverage. To better interpret the preference of edge over corner adatoms, their occupancy as a function of coverage of each non-interacting half unit cell can be examined, as shown in Fig. 4.6. The unfaulted half of the unit cell has a coverage-independent preference of approximately five whereas in the faulted half, edge adatoms are preferred by a factor of approximately two.
Figure 4.6: In the faulted half of the unit cell, left, the preference for edge over corner adatoms is less than that in the unfaulted half.

### 4.3.3 130 K Observations

Figure 4.7: STM Data of thiophene site occupancy at 130 K.
The results of the STM site survey taken at 130 K is shown in Fig. 4.7. The overall trends are similar to those observed at 300 K. One clear difference is the increased preference to bind to edge adatoms. In unfaulted half unit cells, at saturation, only one of every eight thiophene molecules will be chemisorbed to a corner adatom; the rest bind to edge adatoms. The preference for edge adatoms on the faulted half of the unit cell is less than that on the unfaulted half, but still greater than that observed at 300 K.

4.4 Analysis

Figure 4.8: The output from the kMC model, solid lines, to the 300 K STM data, points, was fit to determine the probabilities of adsorption given in Table 4.1.
The four probabilities of the kMC model, $P^c_f$, $P^e_f$, $P^c_u$ and $P^e_u$, were each varied to lower the least squares difference between the model output and the STM data acquired at 300 K. The best fit model output, as well as the corresponding STM data, is shown in Fig. 4.8. An interesting note is that while each of these parameters could be varied to change the output, if the ratios between parameters was kept constant, the output did not change. This does not, however, affect the final interpretation of the data, as that deals with the quotients of the probabilities.

The resulting chemisorption probabilities are given in Table 4.1. In order to turn, for example, the probability of chemisorbing onto a faulted corner adatom, $P^c_F$, into a physically meaningful parameter, it can be interpreted as

$$P^c_F = k^c_F \Delta t.$$  

That is, the product of the rate of reaction with the time the physisorbed molecule spends over the half unit cell. Here the probability of chemisorption to a centre adatom in the faulted half of the unit cell, $P^c_F$, is being considered. However, similar logic can be applied to each probability. Assuming that the rate can be written as a simple Arrhenius equation,

$$P^c_F = A \exp(-E^c_F \beta) \Delta t.$$  

$E^c_F$ is the activation energy barrier to chemisorption at a corner faulted site. For the experimental results presented in Sec. 4.3.1, $T=300$ K.

Eqn. 4.11 contains two unknowns: a prefactor, $A$, and the length of time the molecule spends on one half unit cell, $\Delta t$. While these cannot be determined, the quotient of the probabilities can be used to yield energy barrier differences, assuming
### Table 4.1: Relative adsorption probabilities and corresponding energy barrier differences

<table>
<thead>
<tr>
<th>Site</th>
<th>Relative probability</th>
<th>Energy difference (from F.E.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faulted Edge</td>
<td>7.5</td>
<td>–</td>
</tr>
<tr>
<td>Faulted Corner</td>
<td>4.8</td>
<td>0.011 eV</td>
</tr>
<tr>
<td>Unfaulted Edge</td>
<td>1</td>
<td>0.052 eV</td>
</tr>
<tr>
<td>Unfaulted Corner</td>
<td>0.29</td>
<td>0.084 eV</td>
</tr>
</tbody>
</table>

A and $\Delta t$ are the same for all sites:

\[
\frac{P^F_e}{P^F_c} = \frac{A\exp(-E^F_c/\beta)\Delta t}{A\exp(-E^F_e/\beta)\Delta t},
\]

(4.12)

\[
\frac{P^F_e}{P^F_c} = \exp((E^F_e - E^F_c/\beta).
\]

(4.13)

These energy barrier differences are reported in Table 4.1.

From these energy barriers, a related set of parameters can be generated. This set is dependant on a new value of $\beta$, for $T = 130$ K. These parameters were used to generate a complementary set of output, shown in Fig. 4.9 with the complementary 130 K STM data. One of the significant differences of the predicted low temperature occupancy from room temperature behaviour is the preference for the faulted half of the unit cell. At an average coverage of three molecules per unit cell, the model predicts 2.86 molecules on average on the faulted half of the unit cell.

While the kMC model was able to make a qualitative prediction of the behaviour of this system at lower temperature, the same activation energy barrier differences were unable to describe the site occupancy of thiophene at 130 K as well as they had at room temperature. Some hypotheses for this are given in the next section. Currently, the model parameters are being fitted to the low temperature data.
Conclusion

An extensive STM site survey quantified the occupancy of the four unique bonding sites as a function of coverage. The overall trends agreed with those previously published, that is, the faulted half of the unit cell is preferred to the unfaulted and edge adatoms are preferred to corner. With the extensive site survey, it was shown that the edge to corner preference is much higher on the unfaulted half of the unit cell. The lower activation energy barrier on the faulted half of the unit cell, evident in Table 4.1, could be related to the strain effects discussed in Sec. 3.2.2.

These results were used to fit the parameters of a kinetic Monte Carlo model.
The model includes only activation energy barriers, and a description of the available surface bonds, as a mechanism for determining site selection of thiophene molecules. The excellent fit to STM data demonstrates that at room temperature, site occupation can be described by considering a mobile precursor state and activation energy barriers. On a highly corrugated surface such as Si(111)–7×7, this is an impressive result.

However, the fit to the 130 K STM data indicates that other physical factors dominate at lower temperatures. Benzene has been observed, in the physisorbed state, to prefer edge adatoms at low temperature [17]. This model did not force thiophene to likewise prefer edge adatoms in the physisorbed state. This might explain the under-estimate of the occupation in unfaulted edge sites and the over-estimate of the occupation of faulted corner sites. In order for the model to incorporate this, a physisorbed molecule upon a half unit cell would have $P_e/(P_e + P_c)$ probability of being over an edge adatom. If it was stochastically determined to be over edge adatoms, they would be the only adatoms to which it could bind.

To conclude, while activation energy barriers can accurately describe site occupancy at room temperature, the preferred sites of the physisorbed state must be considered in order to accurately model chemisorption sites at low temperature.
Chapter 5

Mesitylene on Si(111)–7×7

While the Si(111)–7×7 surface is a periodic surface, molecules such as thiophene do not chemisorb to the same sites on each unit cell, and instead form an aperiodic pattern. One notable exception is the physisorbed state of simple aromatics. When 7×7 is held at 50 K and toluene, shown in Fig. 5.1, or chlorobenzene are deposited, these molecules remain in a physisorbed state that appears exclusively above edge adatoms [54].

Small aromatic molecules, such as thiophene or benzene, can easily chemisorb to neighbouring adatoms. The preceding chapters have demonstrated the preference of thiophene to chemisorb to edge adatoms. A STM study of Si(111)–7×7
exposed to benzene and toluene at high coverage showed that approximately half of all faulted halves of the unit cell contain three benzene molecules bound to the three edge adatoms, as shown in Fig. 5.2 a) [55]. Toluene has an additional CH$_3$, or methyl group, on it and the same study observed a preference, at saturation, for corner adatoms. This configuration, shown in Fig. 5.2 b), increases the distance between neighbouring molecules.

Steric hindrance is intermolecular repulsion caused by nearby electron orbitals and was proposed to be the cause of toluene’s increased preference for corner adatoms [55]. Mesitylene, shown in Fig. 5.1, is also closely related to benzene and has, in place of three H atoms, three methyl groups. By moving to a larger molecule, molecule-molecule interactions are expected to be observable in the chemisorption sites. The results of an investigation of mesitylene on Si(111)–7×7 using STM and ab initio calculation are presented here.

![Figure 5.2: At saturation, the most frequent a) benzene chemisorption pattern occurs in approximately 50% of faulted half unit cells and b) toluene pattern occurs in approximately 40% of faulted half unit cells [55]. c) The most common mesitylene chemisorption pattern occurs in approximately 90% of half unit cells. It is impossible to ascertain the exact positions of the methyl groups.](image-url)

The interaction of a single mesitylene molecule with the 7×7 surface can be predicted by appreciating that the methyl groups are relatively chemically inert and
unlikely to react, leaving the aromatic C₆ ring to form the covalent bonds with the surface. Benzene is known to react non-dissociatively with Si(111)–7×7 [20, 15], saturating the dangling bonds of both an adatom and a nearest rest atom [23, 24, 25]. The ring loses its aromaticity and two σ bonds are formed: the two C atoms furthest from each other in the aromatic ring each bind to an adatom and rest atom. Mesitylene is expected to have an identical bonding configuration, that is, that opposite C atoms will each form a covalent bond with an adatom and a rest atom.

5.1 STM Observations

5.1.1 Procedure

Figure 5.3: Mesitylene coverage on Si(111)–7×7 (per half unit cell) as a function of exposure (in milliLangmuir).

Si(111)–7×7 was prepared as described in Sec. 2.4.1. Mesitylene (Sigma-Aldrich, USA) was purified with several freeze-pump-thaw cycles until no further gas evolution
was observed. It was then leaked into the UHV chamber via a precision leak valve, similar to the method described in Sec. 3.1.1. The pressure was kept under $1 \times 10^{-8}$ Torr during all depositions. Again, similar to the thiophene work, the STM data was used to enumerate chemisorption sites as a function of coverage. While this data was not recorded for thiophene on Si(111)–7×7, a plot of the exposure required to generate a given coverage is shown in Fig. 5.3.

5.1.2 Observations

![STM images of mesitylene at low (< 1 molecule per half unit cell) coverage. These two images are not taken at the same area on the surface. Image details: 20 nm × 20 nm, a) +0.8 V, 1 nA. b) -0.8 V, 1 nA.](image)

Low coverage data is presented in Fig. 5.4. Similar to thiophene and benzene adsorption, the dark or missing adatoms are interpreted as mesitylene chemisorption sites. This is explained by the fact that mesitylene is reducing the local density of states, in the energy range probed by the STM, by saturating the dangling bonds. The STM signature in filled and empty state images is very similar to that of thiophene and benzene [26] on the Si(111)–7×7 surface. Thus, a binding geometry of opposite
C–atoms to an adatom-rest atom pair is assumed.

Figure 5.5: At low coverages, shown left, mesitylene prefers edge adatoms. However, when more than two molecules are bound to a unit cell, there is a preference for the corner adatoms. At saturation, the molecules strongly prefer corner adatom bonding sites.

The site occupancy, averaged over the faulted and unfaulted halves of the unit cell, is shown in Fig. 5.5. Interestingly, mesitylene is observed to have no preference for the faulted over the unfaulted half of the unit cell, as shown in Fig. 5.5. This is the first observation of an aromatic hydrocarbon to have this property on the Si(111)–7×7 surface.

A plot of site occupancy on edge and corner adatoms, shown in Fig. 5.5 a), shows a crossing at coverages above one molecule per half unit cell. At low coverages, mesitylene is more often observed on edge adatoms. As the coverage increases past one molecule per half unit cell, corner adatom sites are preferred. This preference is strikingly obvious in high coverage data, such as Fig. 5.6, where predominantly only edge adatoms can be observed.
Figure 5.6: An STM constant-current topographical image of mesitylene at high (> 1 molecule per half unit cell) coverage after 110 mL exposure. Image details: 40 nm × 40 nm, -0.8 V, 0.7 nA.

To confirm the registry of the mesitylene overlayer with the underlying substrate, a small area was desorbed by applying a high voltage while scanning. The surface shown in Fig. 5.6 was prepared and imaged. A region of approximately 10 nm × 10 nm was scanned at 3 V and 1 nA. This voltage was sufficient to desorb most of the mesitylene around the small scan area, leaving behind the 7×7 surface. The new features observable are interpreted as fragments of mesitylene that dissociated during the high voltage scan. The desorbed region, shown in Fig. 5.7, is larger than the scan area. This is likely due to local heating effects that cause desorption outside the scan area. The bright features that remain observable after mesitylene exposure are in proper registry with the edge adatoms, confirming that the molecule is chemisorbing to corner adatoms at high coverage.
Figure 5.7: a) After a 3 V, 1 nA sweep (region shown by white box), mesitylene was desorbed from the surface. Image area: 45 nm × 50 nm, Bias: -0.85 V, Current: 0.8 nA. b) Same image, with lines drawn to show the unit cells of 7×7.
5.2 Ab initio calculations

5.2.1 Procedure

Ab initio calculations were used to characterize chemisorption energies and geometries. Given the structural similarity of mesitylene to benzene and the identical STM signatures at low coverage, configurations well-established for benzene were considered, as in the one schematically shown in Fig. 5.8.

To any given adatom–rest atom pair in the unit cell, mesitylene can bond with either a methyl group closer to the adatom or closer to the rest atom. The chemisorption geometries that were investigated are shown in Fig. 5.9. The Edge1 configuration has the methyl group closer to the adatom, whereas Edge2 has the methyl group closer to the rest atom. This is the same distinction between Corner1 and Corner2.
Figure 5.9: Mesitylene was modelled in the above geometries: a) Edge1, b) Edge2, c) Corner1, d) Corner2 and e) Array. H atoms are not shown for clarity.

5.2.2 Results

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corner1</td>
<td>0.82</td>
</tr>
<tr>
<td>Corner2</td>
<td>1.28</td>
</tr>
<tr>
<td>Edge1</td>
<td>1.31</td>
</tr>
<tr>
<td>Edge2</td>
<td>0.80</td>
</tr>
<tr>
<td>Array</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table 5.1: Binding energies per molecule calculated for the various orientations of mesitylene on the Si(111)–7×7 unit cell. Relative energy differences are accurate to ±0.05 eV.

The binding energies are given in Table 5.1. Once the preferred geometry of a single mesitylene molecule to a corner adatom was known, the full mesitylene array could be modeled. The mesitylene array modeled a saturated Si(111)–7×7 surface with a mesitylene molecule chemisorbed to each corner adatom. The binding energy of this system is reported, normalized for each molecule.
5.3 Application of the kMC Model

Figure 5.10: a) The kMC modelling of thiophene only prohibited further chemisorption to adatoms or rest atoms directly involved in bonding to the thiophene molecule, as shown. b) The mesitylene kMC prohibited bonding to any of the nearest adatoms, shown by the darkened adatoms. Parameters for the mesitylene kMC could only be chosen to match c) low coverage data or d) high coverage data.

At high coverages, mesitylene has been shown to adsorb preferentially to corner adatom sites. One hypothesis regarding the formation of this molecular lattice is that a mesitylene molecule, chemisorbed to a corner adatom, blocks any further chemisorption to neighbouring edge adatoms. That is, the steric hindrance prevents a second mesitylene atom forming a $\sigma$ bond with the nearby edge adatom and with increasing
exposure, the only available sites are the other corner adatom sites.

In order to investigate this formation method of the mesitylene overlayer, the kinetic Monte Carlo simulation (kMC), which was successfully applied to thiophene on Si(111)–7×7 at room temperature, was modified such that chemisorption not only saturated the adatom directly involved in the bonding but the two adatoms closest the rest atom as well. This is schematically shown in Fig. 5.10 a) and b). Over a range of input parameters, the model was unable to reproduce the STM data, as shown in Fig. 5.10 c) and d). Either the low-coverage data could be reproduced (< 1 molecule per half unit cell) with one set of adsorption probabilities or the higher coverage data could be reproduced. Formation of the overlayer, an energetically favourable state, therefore requires desorption and/or hopping from edge adatom sites to corner adatom sites. There is preliminary evidence to support this: STM images of the same scan area do show changes over a period of 20 min. However, more data is required to accurately assess whether the observed changes can account for the formation of the molecular lattice.

5.4 Analysis

With increasing mesitylene exposure, there is an increase in the number of dark or missing adatoms in the empty state STM images. Along with each missing adatom two neighbouring adatoms appear brighter in filled state STM images. This STM signature is similar to that previously reported for thiophene and benzene and it is proposed that mesitylene chemisorbs to the surface via two of the atoms in the C ring, as shown in Fig. 5.8. It has been confirmed that this is an energetically favourable geometry with \textit{ab initio} models.
The most interesting result emerging from the *ab initio* calculations is that the complete mesitylene overlayer yielded a greater binding energy per molecule than two of the geometries, Corner1 and Edge2, of single molecules on the half unit cell. Wolkow et al. reported weaker binding energies of benzene on Si(111)–7×7 at higher coverages [21]. A similar observation was made by [56], however, only for the faulted halves of unit cells.

Assuming a mobile precursor state, the lack of faulted/unfaulted half unit cell preference can be addressed. One possibility is that the molecule simply cannot cross the dimer barrier and is forced to remain in a half unit cell once adsorbed there. This hypothesis could be tested by low temperature STM. Given that the precursor state of benzene was previously observed at 95K [17], by lowering a sample to 90K and depositing mesitylene on it, the mobility of the mesitylene in its precursor state could be observed.

Summary

STM and *ab initio* investigations were conducted on a previously unreported system that saturates the rest atoms and corner adatoms of the Si(111)–7×7 reconstruction, leaving the edge adatoms unsaturated. This unique chemisorption spatial ordering is due to several factors including the well-matched geometry of the aromatic ring to the adatom-rest atom distance and the steric hindrance of the unreactive methyl groups. It is the first aromatic molecule shown to pattern on the Si(111)–7×7 surface and the first molecule shown to form a porous chemisorbed lattice on Si(111)–7×7.
Chapter 6

Mesitylene on Ge/Si(111)

Until now, all systems studied and discussed have involved molecular adsorption on the Si(111)–7×7 surface. The geometric matching between an adatom-rest atom pair is very close to that of the reactive C atoms. Also, while aromatic molecules are electron-rich, the adatoms on the 7×7 surface have only 5/12 filled dangling bonds. While the system of mesitylene on 7×7 was chosen to experiment with intermolecular interactions, deposition of Ge can be used to change the chemical composition and the reconstruction of the surface. Depending on the amount of Ge deposited, it can either substitute for adatoms on the 7×7 reconstruction, grow islands of 5×5 and 7×7 reconstruction, or grow a full 5×5 layer. These three phases, substitution, island and full overlayer, are shown in Fig. 6.1.

Very few studies have been published of adsorbates on the Ge/Si(111)–5×5 surface [57]. It does possess characteristics that make it interesting for the study of site selectivity of aromatic adsorbates. The key difference between it and 7×7 that prompted this study was the elimination of edge adatoms.
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Figure 6.1: a) Below 0.45 ML of Ge, Ge substitutes for Si, preferentially for Si corner adatoms. b) Above 0.45 ML, islands of 5×5 and 7×7 can be observed. Some of these islands contain both reconstructions. c) Above 2.0 ML, the full 5×5 covers the surface.

6.1 Experimental methods

The phase diagram of Ge on Si(111)–7×7 is complex with multiple phases, depending upon the Ge coverage and substrate temperature. A good review can be found in [43]. The 5×5 reconstruction was introduced in Sec. 1.1.1, and schematically shown in Fig. 1.3.

Below 0.45 ML, with an anneal between 350°C to 500°C, Ge substitutes for Si adatoms in the 7×7 reconstruction [58]. Between approximately 0.45 and 2ML, islands of 5×5 and 7×7 are observed [59]. Formation of the Ge–5×5 reconstruction requires between two to four monolayers (1 ML = 7.83×10^{14} atoms cm\(^{-2}\)) of Ge to be deposited upon the Si(111)–7×7 surface. The surface is subsequently annealed to around 350°C to 500°C [59, 9]. The first STM observation of this surface noted that the adatom intensities of the Ge–5×5 surface are much less regular than the Si(111)–7×7 surface, implying a Ge–Si mixture [60].

The Si(111)–7×7 reconstructed was produced and verified with STM. Ge was
evaporated from a custom evaporator, described in Section 2.4.3. To generate the mixed Ge/Si(111)–7×7 surface, Si(111)–7×7 was held at approximately 500° C. Ge was evaporated at a rate of approximately 0.8 ML min$^{-1}$. The amount of Ge was controlled by varying the exposure of the sample to the evaporator. After deposition, the sample was annealed at 500° C for another five minutes.

To investigate the relationship between the amount of Ge deposited and the chemisorption of mesitylene, only the amount of Ge exposed to the surface was varied. All surfaces were allowed to return to room temperature before mesitylene exposure. Each surface was exposed to the 170 mL of mesitylene (1 milliLangmuir = 1 × 10$^{-9}$ Torr sec). This exposure corresponds to a coverage of 0.93 molecules nm$^{-2}$, which is an average of 2.9 molecules on each half unit cell, on the Si(111)–7×7 surface.
6.2 Observations

Figure 6.2: At 0.33 ML Ge, Ge substitutes for Si adatoms. a) 25 nm × 25 nm, +1 V, 1 nA. The substituted adatoms are not apparent in empty state images. Dark (or missing) adatoms are assumed to be unavoidable defects. b) 25 nm × 25 nm, -1 V, 1 nA. The Ge adatoms are the bright adatoms in the corresponding filled state image [61].

Observations of the clean Ge/Si(111)–7×7 surface agreed with those previously published. STM images of coverages below 0.5 ML Ge showed no noticeable changes in empty state images, as shown in Fig. 6.2 a). However, in filled state images, the substituted Ge atoms are evident as shown in Fig. 6.2 b) [61]. At 0.6 ML Ge, islands of 5×5 and 7×7 were grown. On the underlying 7×7 substrate, similar to the surface shown in Fig. 6.2, Ge adatoms substituted for Si adatoms. It is likely the displaced Si adatoms migrate to step edges, as there is no evidence of Si islands. At 2 ML coverage of Ge, the full 5×5 layer was grown.
6.2.1 Ge–5×5 exposed to mesitylene

Figure 6.3: Ge–5×5 after exposure to 170 mL mesitylene. No indication of mesitylene chemisorption can be seen. Image details: 30 nm × 30 nm, +1 V, 1 nA

STM images of the complete 5×5 layer exposed to 170 mL mesitylene are shown in Fig. 6.3. This surface showed no indication of molecular chemisorption. If it had a sticking coefficient equal to that of Si(111)–7×7, a coverage of 1.5 molecules per 5×5 half unit cell (0.93 molecules nm⁻²) would be expected. Both filled and empty state images show a layer with almost no missing adatoms. In a 30 nm × 30 nm STM image of 7×7, one the same size as Fig. 6.3, there would be 143.8 unit cells visible. Given an exposure of 170 mL corresponds to 2.9 molecules on each half unit cell, from Fig. 5.3, approximately 834 molecules would be visible. From this, an upper bound of the relative sticking probability to Ge–5×5 can be calculated as

\[ \frac{1}{834} = 0.0012 \]  

the sticking probability of mesitylene on Si(111)–7×7.
6.2.2 DAS islands exposed to mesitylene

![Figure 6.4: A surface prepared with 0.6 ML Ge exposed to 170 mL mesitylene. 60 nm x 60 nm a) +1 V, 1 nA. b) -1 V, 1 nA. Mesitylene chemisorption sites are easier to see on and off the islands in c), the I channel, which approximates the derivative of the image. Mixed islands of 5×5 and 7×7 are indicated.](image)

STM data of a surface with islands of 5×5 and 7×7, after mesitylene exposure, is shown in Fig. 6.4. The 5×5 region shows no sign of molecular adsorption. The 7×7 island regions and substrate regions indicate limited mesitylene chemisorption. The average measured coverage of this surface is 0.11 molecules nm$^{-2}$ (0.34 molecules per 7×7 half unit cell).
6.2.3 Sub-monolayer Ge exposed to mesitylene

Figure 6.5: STM data of surfaces exposed to 170 mL mesitylene after a) 0 ML Ge, b) 0.08 ML Ge, c) 0.16 ML Ge and d) 0.33 ML Ge deposition.

Below the island growth regime, Ge preferentially substitutes for Si adatoms. Fig. 6.5 shows STM data of mesitylene exposure to four different surfaces: 0 ML Ge, 0.08 ML Ge, 0.16 ML Ge and 0.33 ML. The mesitylene pattern clearly observed with 0 ML Ge exposure is hindered and finally prohibited as the amount of Ge in the underlying reconstruction increases.
6.3 Analysis

Three Ge-induced phases, substitution, island and full 5×5 layer, were grown and exposed to 170 mL of mesitylene. No evidence was observed for mesitylene chemisorption on the Ge/Si(111)–5×5 surface. On a mixed surface that included 7×7 and 5×5 reconstructions, chemisorption appeared to favour the 7×7 areas. At sub-monolayer coverages, the amount of Ge determined the coverage of mesitylene on the surface. That no mesitylene is observed to chemisorb on the 5×5 surface means that either the activation energy for chemisorption is greater than the desorption energy or that the final binding energy is greater than the energy of the two isolated systems (the surface and the molecule).

Amongst other things, the final binding energy would depend upon the bond energy of the Ge–C bond. The single-crystal Ge(001) surface has been studied more frequently for both atomic [62, 63] and molecular adsorbates [64, 65, 66, 67, 32]. One result from these studies is a comparison of the bond strength of the Ge–C to the Si–C bond. TPD data of C₂H₂ on Ge(100) yield a binding energy of 1.3 eV, approximately 0.6 eV less than that of C₂H₂ on Si(100) [68]. Furthermore, a PES study that exposed Si(100) to 300 L of thiophene required 13,000 L of thiophene on a Ge(100) surface to generate an equivalent spectrum [32].

Ge reconstructs into 5 × 5 when it is compressed [69]. This is facilitated by the lattice mismatch with Si. Chapter 3 reported the surface strain required for thiophene chemisorption as approximately 0.4 eV. It is possible that substitution of a Ge atom in the Si surface induces additional strain that increases the activation energy barrier until it is highly improbable at the coverages that were investigated.

While strain is one possibility for the reduced sticking coefficient, another is the
Ab initio models have been considered for a) a bare Si(111)–7×7 surface and b) mesitylene on Si(111)–7×7 but by substituting c) a Ge atom for a Si adatom, shown by the green atom, the binding energy of d) mesitylene on a Ge adatom can be calculated.

The electronic difference between Ge and Si on the Si(111) surface. This difference is most clearly seen in Fig. 6.2 b). The Ge atoms appear much brighter in the filled-state STM images, which suggests they might have a much higher local electron density. An electron-rich adsorbate, such as mesitylene, is unlikely to favourably bond to an electron-rich site.

To determine whether the observed Ge passivation is thermodynamic or kinetic, ab initio calculations can model the total energy of mesitylene on a surface with a substituted Ge adatom, as shown in Fig. 6.6. The final binding energy could then be compared to that of mesitylene on a pure Si(111)–7×7 surface. The surface strain would indicate whether the reduced sticking coefficient is due to structural effects. Finally, to address whether Ge has a higher density of states that might impede mesitylene chemisorption, a local density of states of the Ge adatom could be compared to a neighbouring Si adatom. These calculations will be performed in the near future by our collaborators.
Summary

The 5×5 layer grown on Si(111)–7×7 has the adatom–rest atom separation as the 7×7 reconstruction. Given the ease at which mesitylene chemisorbs to the Si(111)–7×7 surface, it was expected that mesitylene would be equally likely to chemisorb to the 5×5 reconstruction. That it does not chemisorb readily to the Ge/Si(111) systems indicates that there are factors, other than simple geometric matching, strongly affecting the sticking coefficient. As mentioned above, \textit{ab initio} calculations will be performed by R.H. Miwa and will hopefully elucidate both the electronic differences between a Ge adatom and a Si adatom, as well as answer whether a mesitylene molecule chemisorbed to a Ge adatom is thermodynamically favourable.
Chapter 7

Conclusions

The foundation for our modern understanding of molecule-surface interaction was laid around the turn of the twentieth century by Irving Langmuir. In a seminal article from 1916, he presented the idea that the constituent atoms of a molecule can interact with surfaces the same way atoms within a molecule interact, via covalent bonds [70].

Sixty-five years later, the scanning tunneling microscope was invented by Binnig and Roher. With the ability to probe surfaces at sub-nanometer resolution, the STM provided real-space data of a variety of surface reconstructions and individual molecules on a host of conducting surfaces [71]. Many STM investigations have probed the reactions of molecules with surfaces, especially semiconductor surfaces such as Si [72, 73, 74, 75]. The ability to control molecular placement and attachment on a semiconductor surface is appealing from a practical standpoint because it is considered to be one step in incorporating molecules as components in electronic devices [1, 76]. Implementing molecular self-assembly into useful components on a Si surface is a long way off and requires, in part, an understanding of how ensembles of molecules bind to Si surfaces.
Results

This thesis examined two molecules, thiophene and mesitylene, on DAS surface reconstructions.

The thiophene work was prompted initially by an observation that certain sites on the surface were preferred for chemisorption. An extensive survey of average site occupancy as a function of coverage was conducted with STM. Adsorption sites were identified as being on either the faulted or unfaulted halves of the unit cell and on either corner or edge adatoms. The faulted edge adatom site is most strongly favoured as an adsorption site. STM images collected at 130 K showed similar trends but with a much stronger preference for edge adatoms.

*Ab initio* calculations revealed that all bonding sites had almost equal binding energies, implying that all site selectivity is due to the kinetics of chemisorption. A kinetic Monte Carlo model was written to address the hypothesis that activation energy barriers determined the site occupancy on Si(111)$-7 \times 7$. It was found that, by fitting the differences in activation energy barriers, the output of the model could be fit to the 300 K STM data. It was expected that these barriers could predict the behaviour of the system at different temperatures. The output was compared to 130 K STM data. The agreement was not acceptable to validate this low temperature prediction. One possible reason is that the physisorbed state prefers certain sites over another and that this preference is stronger at lower temperatures.

Mesitylene was also studied on the Si(111)$-7 \times 7$ surface. The same STM statistics, that is, site occupancy as a function of coverage, were collected. It was found that at low coverages, mesitylene follows the same trends as thiophene. However, when the coverage exceeds one molecule per half unit cell, the molecules begin to interact and
mesitylene starts to show a strong preference for corner adatoms. When the surface is saturated, an almost complete preference for corner adatoms is observed. Over ten years ago, Hamers and coworkers showed, under UHV conditions, that the underlying dimer structure of Si(100) can be used to pattern cyclopentene [77]. This is the first analogue on the Si(111)–7×7 surface.

Finally, to explore the sites selectivity on a related surface, mesitylene was deposited on a Ge–5×5 layer, grown on the Si(111)–7×7 surface. However, no indication of mesitylene was observed on the 5×5 layer. When the amount of Ge was decreased, a mixed-phase surface could be grown. Upon this surface, chemisorbed mesitylene was observed on the 7×7 reconstructed surface. Sub-monolayer amounts of Ge substitute for Si adatoms and, by decreasing the amount of Ge–substituted adatoms, a full mesitylene molecular lattice could again be observed. These observations indicate that mesitylene does not bond readily to Ge atoms.

These experiments probed the interaction of the molecules with the available bonding sites on the Si(111)–7×7 surface. The first extensive STM survey of site occupancy of aromatic molecules allowed a kinetic Monte Carlo model to validate site selectivity at room temperature as a function of different activation energy barriers. The first aromatic molecule to pattern on Si(111)–7×7 at room temperature was discovered. Finally, the unexpected passivating effect of Ge was discovered.

Current and Future Work

These investigations have left open several pathways for further experiments, some of which are being currently pursued. Two different theoretical groups are investigating
methods for calculating the activation energy barriers of thiophene on the Si(111)–7×7 surface: R.H. Miwa at the Universidade Federal de Uberlândia in Brazil and P. Jelenik at the Institute of Physics, Academy of Sciences of the Czech Republic. As well, they are attempting to accurately model the van der Waals force in order to explore the favourable positions for molecules in a physisorbed state on the surface. These numbers could be inputted in the existing kMC model and then compared to the existing STM data.

The question of mesitylene bound to a Ge adatom is currently being explored by R.H. Miwa. It is expected that the binding energy can be used to determine whether the observed passivation is due to thermodynamics or kinetics.

The molecular lattice formed by mesitylene on Si(111)–7×7 is the most exciting discovery of the work presented in this thesis. One extension of this work would be to demonstrate its ability to direct the adsorption sites of other species. At sub-monolayer coverages, C_{60} does not adsorb in one specific site within a unit cell of Si(111)–7×7 surface [78]. It is possible that a mesitylene molecular lattice could itself template adsorbed C_{60} molecules on the surface.
Bibliography


Appendix A

Ultra High Vacuum

The time for saturation of a Si(111)–7×7 reconstructed surface in atmosphere can be approximated assuming a N$_2$ environment ($m = 28$ amu) that reacts with the surface with a sticking coefficient of 1. Assuming that the average kinetic energy of $N$ molecules is $\frac{3}{2}kT$,

$$ P = \frac{F}{A}, $$

$$ = \frac{N\delta p}{A}, $$

$$ \approx \frac{N\delta p}{A\delta t}, $$

$$ \delta t = \frac{N\delta p}{PA}, $$

$$ = \frac{2N\sqrt{3mkT}}{PA}. $$

$\delta p$ has been assumed to be $2\delta v$, from the kinetic energy at room temperature. Requiring nine molecules to saturate a half unit cell of area $(2.688 \text{ nm})^2 \times \frac{\sqrt{3}}{4}$, the size of a Si half unit cell,

$$ \delta t = \frac{2\delta \sqrt{3(28 \text{ amu})(0.025 \text{ eV})}}{(1 \text{ atm})(3.13 \times 10^{-18} \text{ m}^2)}, $$

$$ = 92 $$
By moving to a vacuum with a base pressure of $5 \times 10^{-11}$ torr,

$$\delta t = 1.5 \text{ hr.}$$

(A.8)

In practice, the $7 \times 7$ surface remains clean for much longer because the sticking coefficient is not unity, however this simple calculation illustrates the need for an ultra-high vacuum (UHV) environment.
Appendix B

Ab initio calculations

The calculations were performed by R.H. Miwa and G.P. Srivastava using the supercomputer network at the University of Exeter. They were done in the framework of DFT, [45] using the generalized gradient approximation due to Perdew, Burke, and Ernzerhof [79]. The electron–ion interaction was treated by using norm–conserving, \textit{ab initio}, fully separable pseudopotentials [80]. The Kohn–Sham wave functions were expanded in a combination of pseudoatomic numerical orbitals [81]. A double zeta basis set, including polarization functions (DZP), was employed to describe the valence electrons [82]. The self–consistent total charge density was obtained by using the SIESTA code [47]. The Si(111)–7×7 surface was simulated using the slab method, with a supercell containing six monolayers of Si with a 7×7 surface unit cell plus a vacuum region of 12 Å. A mesh cutoff of 120 Ry was used for the reciprocal–space expansion of the total charge density, and the Brillouin zone was sampled by using one special $k$ point. Two hundred and ninety eight Si atoms were used and, in the bottom layer, 47 dangling bonds were saturated with hydrogen atoms. The convergence of the results was verified with respect to the number and choice of the special
\textbf{APPENDIX B. AB INITIO CALCULATIONS}

\textit{k} points using up to four \textit{k} points. Some results of equilibrium geometry and surface were checked by using a plane wave basis set with an energy cutoff of 18 and 25 Ry. Equilibrium geometries were obtained by full relaxation of the four topmost Si layers and the adsorbed molecule. A force convergence criterion of 20 meV/Å was used.