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OF OXIDE CLUSTER NUCLEATION AND
OXIDATION-INDUCED ETCHING
ON SILICON SURFACES

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Presented in Partial Fulfillment of the Requirements for
the Degree of Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Jeffrey Vance Seiple, M.S.

* * * * *

The Ohio State University
1996

Dissertation Committee:
Professor Jonathan Pelz, adviser
Professor Charles Ebner
Professor Gregory Lafyatis

Approved by

[Signature]
Adviser
Department of Physics
ABSTRACT

Ultra-high vacuum, scanning tunneling microscopy (UHV-STM) has been used to investigate the initial stages of silicon oxidation in an effort to understand the evolution of surface morphology in the technologically critical Si/SiO₂ system. Oxidation conditions included silicon substrate temperatures between 20°C and 940°C, oxidation pressures between 2x10⁻⁹ and 5x10⁻⁶ torr, and doses up to 2000 Langmuir. Focus has centered on a regime of intermediate temperature and pressure conditions (590-740°C, 3x10⁴-2x10⁷ torr) where exposure to oxygen simultaneously nucleates an oxide film as well as etches the silicon surface via the evolution of volatile SiO. Under these conditions localized “clusters” of oxide nucleate on the surface and prevent the immediately underlying silicon from etching. This type of “nano-masking” tends to roughen the surface since the clean areas between the oxide patches are being continually etched downward while the silicon under the oxide patches remains at its original height.

In an effort to quantify the oxide nucleation behavior in this roughening regime, STM was used to count individual, nucleated oxide clusters. This is the first study to count such clusters and use the results to directly test atomic-scale models for silicon oxidation. The experimental findings show that at early doses, < 200 L, the nucleation of clusters increases, but at higher doses the nucleation of new oxide clusters is suppressed.
Concurrently, however, the average cluster height increases linearly with dose implying that the vertical etching between the clusters is approximately constant in time. Taken together these two findings are inconsistent with a single-species oxidation model, but are consistent with a dual-species oxidation model.

By using a single set of reasonable activation energies and prefactors, rate equation analysis and Monte Carlo simulations of the dual-species model were found to be consistent with the measured temperature and pressure dependent data on both Si(001) and Si(111) surfaces. With this model, cluster densities were then predicted under varying oxidation conditions and verified with subsequent experiments. These experiments suggest the possibility of exploiting oxide nucleation kinetics to gain greater control of the fabrication of gate oxide dielectrics or patterned oxide masks for the microelectronics industry.
Dedicated to my Family

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VITA

May 8, 1968 ................................................. Born - Easton, PA

May 30, 1990 .................................................. A.B. Physics and Mathematics
Colgate University

August 29, 1993 ............................................. M.S. Physics
The Ohio State University

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and etching of the Si(111) 7x7 surface observed with scanning tunneling
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CHAPTER 1

INTRODUCTION

1.1 Motivation for study of the Si/SiO₂ system

The oxidation of silicon surfaces is a process of critical importance in the microelectronics industry.¹²³⁴⁵ The oxides grown fall into two basic categories, the thin, high-quality gate oxide, and the thick field oxide. The field oxides can be patterned through a photolithography process and subsequent HF etch.³ These patterned oxides are then used to mask the silicon substrate for subsequent dopant diffusion. In this way devices may be patterned onto a silicon wafer by delineating specific n- and p-type doping regions. The gate oxide is used as the insulating layer in the important Metal-Oxide-Semiconductor Field-Effect-Transistor (MOSFET).³⁴⁵ This gate oxide connects the regions of n- or p-type doping establishing the channel region for electrical activity in the transistor. Quite often it is the quality of the gate oxide and particularly the quality of its interface with the silicon substrate that will determine the performance of the resulting device.¹²
Given the critical roles these oxides play, it is not surprising that much research has focused on how oxide forms on the silicon surface under different oxidation conditions. In practice it has been found that the Deal-Grove oxidation model can accurately predict the thickness of oxides grown with either dry oxygen or with water vapor for oxides thicker than 300 Å. To date, this macroscopic model alone has been sufficient for fabricating many modern devices. In the microelectronics industry, however, smaller devices are faster, and faster is more lucrative. Thus today ultra large scale integrated (ULSI) device technology increasingly demands that individual device components be made smaller, insulating layers be made thinner, and that all processing be done at lower temperatures than previously required. These new requirements translate into an increased need for a microscopic understanding of the initial stages of silicon oxidation at reduced temperatures. This understanding is important to the controlled growth of ultra-thin insulating SiO₂ films at low temperatures. It is also crucial to the prediction and control of surface roughening during transient exposure to residual oxygen and/or water vapor in modern integrated processing chambers.

This microscopic understanding is also interesting from a fundamental standpoint. For years scientists have been striving to understand the nucleation and growth of thin films in a variety of systems. It is therefore surprising that relatively little is known about the atomic-scale aspects of oxide nucleation and growth on silicon considering the importance of the system. For example, fundamental kinetic information such as the mechanism for oxide film growth at the sub-monolayer regime
is not well understood. Similar questions to those asked in epitaxial film growth can be asked of the oxygen/silicon system as well: Does an oxide film form layer-by-layer or does it nucleate clusters or patches of stable oxide first? How does the film formation depend on growth conditions? If there is 2D oxide cluster nucleation, is it a diffusion limited growth process, and if so what is the diffusion energy for oxygen on the silicon surface? Similarly, what are the nucleation and growth energies for oxygen to form these clusters? Questions like these have remained essentially unanswered although some groups have made estimates of the relevant energies involved. In addition to these questions, the reactive nature of oxygen/silicon system can cause surface morphology changes due to oxidation-induced etching. This fact introduces added complexity over simple nucleation and growth systems and poses even more questions: Does the changing step morphology affect subsequent nucleation? Does the etched surface change the diffusion rates for surface species? Does the etched morphology introduce strain effects that should be considered? If questions of this nature could be answered, it would be of fundamental interest to actually formulate an atomic-scale model that would explain the complex behavior of oxide nucleation as well as quantitatively account for oxidation-induced etching of the silicon surface under low oxygen partial pressures. Gaining such a fundamental understanding could be useful for avoiding film growth in a roughening regime as well as for controlling the growth of high quality, thin oxides in potentially lower temperature regimes than are currently used in practice.
In addition to determining conditions to optimize high quality films, we may be able to use a successful model to predict and control roughened surfaces and interfaces for further fundamental studies within a roughening regime. These studies may include quantifying MOS capacitor breakdown voltage or quantifying electron mobilities in a roughened MOSFET channel region as functions of the roughness created. Finally, there may be an entire range of applications not yet envisioned, but that may nevertheless benefit from a knowledge of the fundamental parameters associated with thin film nucleation and growth in the oxygen/silicon system.

1.2 Introduction to the silicon substrate

Before discussing oxidation, a brief review of the silicon substrates used in these studies will be presented. For more detailed information the reader may wish to refer to some well known references on the silicon surface.\textsuperscript{14,15,16} Although many crystalline planes of silicon have been studied, for this manuscript only the most common (001) and (111) vicinal planes of silicon will be discussed. The Si(001) surface is the substrate used most commonly in industry, and hence will be the primary focus throughout this paper. The Si(111) surface will also be discussed since much of the early work on silicon oxidation at the microscopic level was carried out on this crystalline plane.

Silicon is the most common and most abundant elemental semiconductor on earth. Structurally, the bulk material has the diamond crystal structure which is face-centered
cubic (fcc) with an atomic basis of two. Figure 1.1(a) shows a unit cell of bulk silicon. The length of a side of this cube, $a$, is defined as the lattice constant which for silicon is 5.43Å. One of the atoms of the basis is naturally located at a normal fcc corner location (0) while the second atom in the basis is located at the vector $a/4(\hat{x} + \hat{y} + \hat{z})$ relative to the former. Figure 1.1(b) defines the crystallographic coordinate system that will be referred to throughout this paper. As a standard notational convention, it should be noted that $(xyz)$ is the plane normal to the $[xyz]$ direction, and that $\{xyz\}$ is the set of all equivalent planes to the $(xyz)$ plane and $<xyz>$ is the set of all equivalent directions to the $[xyz]$ direction. The equivalency arises simply from the cubic symmetry of the structure. The $\{100\}$ set of surfaces is made up of the faces of the cubic unit cell, the $\{110\}$ surfaces run diagonally through four corners of the cube, and the $\{111\}$ set of surfaces is made up of the planes running diagonally through three corners of the cube as shown schematically in Fig. 1.1(c). It should be noted that the face-centered and basis atoms have been left out of the schematic in Fig. 1.1(c) for clarity.

With the face-centered atoms included, it easy to see that the spacing between $\{111\}$ layers is just one third of the cube’s diagonal length, or $a/\sqrt{3} = 3.135$ Å. It should be noted, however, that the basis atoms do not quite lie in the same $(111)$ plane as the fcc atoms but are displaced a small normal distance of 0.784 Å. Since this distance is small compared with the 3.1 Å separation of the fcc $\{111\}$ planes, it is the usual convention within the scanning tunneling microscopy (STM) community to include these basis atoms with the others and refer to the $\{111\}$ planes in general as bilayers. This convention is
also based on the energetics of the system in that a half bilayer termination would result in a very high energy surface with three dangling bonds per atom. Thus complete bilayer termination is energetically more favorable from a bonding standpoint. As a matter of practicality, then, a “single” step height in an STM image of Si(111) actually refers to the spacing between bilayers (BL), 3.135 Å. For the spacing between fcc {100} planes, the separation is clearly \( a/2 = 2.716 \text{ Å} \) (Fig. 1.1). In this case, however, since the basis atoms lie half way between the usual fcc {100} planes, they are not grouped with the others. In addition, the symmetry along this direction, implies that each layer of the basis atoms would be energetically degenerate (two dangling bonds per atom just rotated 90°). Therefore with the basis atoms included the spacing between {100} planes in silicon becomes \( a/4 = 1.358 \text{ Å} \) as can be clearly seen in Fig. 1.1. Thus in STM images, single step heights on Si(001) are 1.358 Å or 1 monolayer (ML) high.

Samples used for most studies are commercially obtained and have been cut from a large silicon boule. It turns out that this process and subsequent wafer polishing introduces a miscut to the resulting sample. The miscut manifests itself by introducing atomic steps on the surface. These atomic steps separate terraces of the perfect crystalline termination (e.g. the (001) plane), and the average terrace width between these steps is determined by the angle (or magnitude) of miscut away from the ideal crystalline plane. Figure 1.2 schematically illustrates examples of miscut on (a) the Si(001) surface and (b) the Si(111) surface and how the angle can be calculated based on terrace length (or step spacing) and step height. If the miscut angle is very high (\( \approx 2-4° \)), the steps formed are
often double atomic steps high. It turns out that double steps have lower energy than two isolated single steps, so this fact facilitates the transition to from single- to double-height steps. The reason that double steps are not spontaneously formed at lower miscuts, however, is because the single steps on Si(001) allow for strain relaxation in the surface stress that is enhanced by having large terraces of a particular surface reconstruction. In addition, entropy considerations tend to work against the formation of ordered, double-height steps. The studies presented here will focus primarily on the low miscut (< 1°), single-stepped surfaces. One further note which will be expanded upon below is that not just the magnitude of miscut affects the resulting vicinal surface, but also the direction of the miscut.

The surfaces noted in Fig. 1.1 would be the surfaces if the crystal were ideally “bulk terminated.” For Si(111), this bulk termination has not been directly observed since it has been shown that cleaving a Si(111) sample in a UHV environment at room temperature leads directly to the formation of a 2x1 reconstructed surface. Similarly, the Si(001) bulk termination has not been observed because the Si(001) plane is not a cleavage plane. As a result, it may be that this surface also reconstructs even at arbitrarily low temperatures. In any case, the surfaces dealt with most often have been prepared through some type of thermal cleaning. This is usually the case because the wafer is cut in air, and the new wafer surface forms a thin native oxide layer. To image the bare silicon surface with STM, this oxide layer must be removed. To accomplish this, the Si wafer is heated to temperatures above 900°C in a UHV environment at which point this oxide begins to desorb. Upon cooling down, the surface has many free dangling bonds.
and hence a high surface free energy. In order to minimize this surface free energy, the surface utilizes the available thermal energy and reconstructs, reducing the number of dangling bonds at the slight expense of some strain energy. This new reconstructed surface once formed will stay clean for many hours in a UHV environment, providing ample time for study.

The reconstruction that forms is very much dependent on the crystalline surface being examined. The (001) surface reconstructs to form a 2x1 structure as shown in Fig. 1.3. In this reconstruction, two adjacent silicon atoms will bend toward each other to form a covalent bond, creating a dimer. This reduces the number of dangling bonds on the bulk terminated surface by a factor of two. Adjacent pairs of atoms also form dimers and align to form long dimer rows across the surface. A top-view greyscale STM image of a Si(001)-(2x1) surface will generally resolve these rows as seen in Fig. 1.3(b), and can sometimes even resolve single dimers within these rows (the boxes in Fig. 1.3(b)).

Numerous interesting studies have shown that the dimer reconstruction on Si(001) is not as straightforward as Fig. 1.3(a) may indicate. Wolkow found experimental support for earlier calculations that suggested the dimers of the 2x1 reconstruction are not symmetric, but rather oscillate back and forth between tilted orientations (Fig. 1.3(c)). At room temperature this oscillation is believed to be so fast that the dimers just appear symmetric in typical STM images. By cooling the Si(001)-(2x1) surface to low temperatures, Wolkow found that buckling did in fact become more prevalent. In addition, defects can lock in a particular buckling configuration as seen next to the step in Fig. 1.3(b). Since individual dimer resolution is often difficult to obtain, buckling is
often useful for obtaining lateral spacing within a dimer row when interpreting STM images.

Another interesting point about this surface is that at each monatomic step, the direction of these dimer rows switches by 90°. The reason for this 90° switch can be seen clearly from Fig. 1.1, where the tetrahedral bonding symmetry of the crystal is evident. Because of this symmetry, atoms in the adjacent crystalline layers (1 ML or $a/4$ apart) have bonds that are rotated by 90°, so that when the dimer is formed it will be orthogonal to dimers in the immediately adjacent layers. It should be noted that only the surface layers undergo this dimer reconstruction.

The orthogonal dimer rows on adjacent terraces create a large surface anisotropy. The terraces themselves are sequences of alternating 1x2 and 2x1 domains, creating anisotropic stress that can extend into the bulk\textsuperscript{22} as well as anisotropic diffusion for atoms deposited on these terraces.\textsuperscript{23,24} The anisotropy is also manifested by the steps. As can be seen from Fig. 1.4, the 90° rotation (or dimer row orthogonality) on adjacent terraces will result in a step segment that terminates either at the end or the side of a dimer row on the upper terrace. If the dimer rows on the upper terrace run parallel to the step segment direction then that step is called an $S_A$ step segment.\textsuperscript{18} If the dimer rows terminate perpendicular to the direction of a step segment then that step is called an $S_B$ step segment.\textsuperscript{18} Furthermore, if the miscut is in a [110] direction, then one may refer to the steps in general as being either $S_A$ or $S_B$, since each step will be almost entirely made up of a single type of step component. If the miscut is directed along the [010] direction, however, dimer rows will terminate at 45° to the overall step direction, and the steps will
be isotropic with respect to each other, having equal components of $S_A$ and $S_B$ step segments.

It has been shown by many authors that $S_A$ and $S_B$ steps have distinctly different properties in terms of energetics in general.\textsuperscript{18,25,26,27,28} This research has shown $S_A$ step segments are lower in energy than $S_B$ segments and that as a result kinks are much easier to form on $S_B$ steps than on $S_A$. It should be noted that a kink on an $S_B$ step is simply an $S_A$ step segment with a corner and vice versa. For example, Swartzentruber \textit{et al.}\textsuperscript{26} have measured anisotropic energies of 0.028 eV/atom at an $S_A$ step and 0.090 eV/atom at an $S_B$ step. Calculations by Chadi have shown the same preference for lower energy $S_A$ steps, but with step energies of 0.01 eV/atom ($S_A$) and 0.15 eV/atom ($S_B$).\textsuperscript{18} As a result, $S_B$ steps are much more “wavy” than $S_A$ steps as can also be seen in Fig. 1.4(b). Recent work by Jones \textit{et al.}\textsuperscript{28} has shown that this waviness can be enhanced through strain effects. In addition, when growing Si epitaxially, the islands that form show anisotropic shapes both when quenched to room temperature from growth as well as after annealing in UHV.\textsuperscript{29,30,31} The anisotropic ratios of $S_A$ segments to $S_B$ segments of an island are as high as 15:1 (kinetically limited) and about 3:1 after annealing (thermodynamically limited).\textsuperscript{31} This indicates that $S_A$ steps have lower energy thermodynamically than $S_B$ steps, and that kinetically $S_B$ steps have a much higher propensity for adatom attachment.

Even reconstructed surfaces are not perfect. In all cases a certain number of defects form during the surface reconstruction. For the Si(001)-(2x1) reconstruction that forms dimers on the top-most terraces, common defects involve dimers that are physically absent or “missing” from the surface. These missing dimers appear as dark
holes in the reconstruction and should be distinguished from reacted dimers which may also appear dark in STM images (see discussion § 2.2.2). Depending on the actual dimers or atoms missing in the surface layer, these defects are labelled A-, B-, or C-type.\textsuperscript{32} If there is a single missing dimer, the defect is A-type, double missing dimers adjacent to each other are a B-type defect, and a C-type is believed to be two half missing dimers as shown in Fig. 1.5(a).\textsuperscript{32} Another type of defect that may occur on the Si(001) surface is an anti-phase boundary in the 2x1 reconstruction as shown in Fig. 1.5(b). For typical UHV studies of the Si(001) surface, the total defect density is on the order of 2\%, mostly coming from 'A-' and 'C-type' defects. The role these defects may play during oxidation will be addressed in section 4.4.4.

The Si(111) bulk terminated surface also reconstructs when heated to elevated temperatures. The most stable reconstruction commonly examined is the 7x7 reconstruction shown in Fig. 1.6 along with two common metastable reconstructions, the 5x5 and 9x9.\textsuperscript{33} A 2x1 structure may also form which is different than the Si(001)-(2x1) reconstruction and not as stable on the Si(111) surface. In fact, Feenstra and Lutz have shown that the Si(111)-(2x1) spontaneously forms after cleaving a Si(111) surface in vacuum.\textsuperscript{10} Then as the sample is heated, the surface passes through a 5x5 reconstructed state and then finally forms the 7x7 reconstruction which is energetically most favorable.\textsuperscript{10} The 7x7 structure is considerably more complex than the Si(001)-(2x1) structure and is not formed unless temperatures exceed \(-600\)°C.\textsuperscript{20} The atomic configuration for this structure, the dimer-adatom-stacking fault model (DAS), was originally reported by Takayanagi et al. in 1985.\textsuperscript{24} The unit cell of the reconstruction is
made up of 102 total atoms. Of these, 12 are in the topmost layer and are referred to as adatoms, 42 atoms are in the next layer (the upper layer of the bilayer) and 48 atoms are in the bottom layer of the bilayer. The 12 adatoms are the bright atoms imaged in greyscale STM images of Si(111) (Fig. 1.7), and under optimal conditions, the six exposed "restatoms" of the next 42 atoms may also be imaged in the six hollows between the adatoms. The absence of top-layer atoms at the corners of the 7x7 cell are called "corner holes." The stacking fault is evident in that the atoms of the left triangular sides (the faulted side) of the DAS reconstructions in Fig. 1.6 cover the atoms in the first bulk layer, while those from the right triangular side do not. In STM images, the faulted half of the unit cell will appear generally brighter than the unfaulted half if a negative sample bias is used (see section 2.2). Like the 2x1 surface, defects are also present on this surface, usually in the form of a missing adatom as shown by the arrow in Fig 1.7. or occasionally a crystalline grain boundary. Again, the roles these defects play will be discussed in a separate section.

An interesting side note about the DAS reconstructions is that the surface density of atoms changes between the 5x5, 7x7, and 9x9 structures. For the 5x5 reconstruction, 5 times 5 times a basis of 2 equals 50 total atoms in the surface reconstruction, and in fact, counting will yield 50 atoms in the DAS model. This implies that the surface density of atoms for the reconstructed surface is the same as that for the bulk terminated surface. For the 7x7 reconstruction, however, 7 times 7 times a basis of 2 equals 98 atoms which is four atoms short of the known number of 102 found in the DAS model. This tells us that the 7x7 structure is more dense than the bulk terminated surface and that
surface holes (possibly in the form of missing adatoms) must exist in order to compensate for the different density. This density difference may also facilitate the formation of the 5x5 reconstruction before the 7x7 when slowly increasing the temperature of a freshly cleaved Si(111) sample.\textsuperscript{20} For the 9x9 reconstruction, the situation is even worse with 9 times 9 times a basis of 2 equaling 162 atoms, but the measured number from the DAS model is 172.

\textbf{1.3 Review of Silicon Oxidation}

Many reviews of the electrical behavior of the Si/SiO\textsubscript{2} interface are available, but few focus on the molecular aspects of silicon oxidation. A recent review has been compiled by Engel in 1993 which focuses on both atomic and molecular oxygen interactions with the (001) and (111) silicon surfaces.\textsuperscript{35} In the interest of staying with the microscopic aspects of silicon oxidation only a few representative atomic-scale studies and those with atomic-scale implications will be presented here. The following sections are divided as follows: section 1.3.1 reviews the earliest work which was done on Si(111)-(7x7) at room temperature, section 1.3.2 reviews room temperature Si(001)-(2x1) oxidation, section 1.3.3 discusses papers addressing the elevated temperature phase diagram of silicon oxidation, section 1.3.4 discusses elevated temperature work on Si(111), section 1.3.5 reviews elevated temperature Si(001) oxidation, and finally section
1.3.6 summarizes some of the key findings and some still outstanding questions regarding silicon oxidation.

1.3.1 Room Temperature Si(111)-(7x7) Oxidation

Since the early 1980's, many studies of the initial stages of Si(111)-(7x7) have been done. Most of the early studies did not have atomic-scale resolution, but nevertheless were able to infer atomic-scale information such as bonding coordination, binding energies, etc. Techniques used included high-resolution core-level spectroscopy with synchrotron radiation, Auger electron spectroscopy (AES), work function measurements, X-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), low energy electron diffraction (LEED), temperature-programmed desorption (TPD), and laser-induced thermal desorption (LITD).

Hollinger and Himpsel found that four distinct core-level shifts occurred during silicon oxidation within the first monolayer of coverage. They attributed these shifts to silicon atoms bonded to 1, 2, 3, and 4 oxygen atoms. They found that upon annealing surfaces exposed to room temperature oxygen, the number of silicon atoms bound to 1 or 2 oxygen atoms decreased while the number bonded to 3 or 4 oxygen atoms increased. At very low coverages (<0.2 ML), only one core-level shift was found, and it was attributed to one oxygen atom in a bridge-bonded site between two silicon atoms.
Tabe et al. found that oxidation proceeded via a fast uptake followed by a saturation and a slow uptake regime. They found that the slow uptake regime could be enhanced by oxidizing at higher temperatures consistent with the idea that oxygen atoms can more easily insert into back bonds at higher temperatures hence leaving more surface dangling bonds available for initial sticking. The LEED studies by this group indicated that a 7x7 $\rightarrow$ 1x1 transition occurred at a specific oxygen coverage regardless of temperature. The 1x1 LEED pattern was not attributed to an ordered overlayer of oxide, but rather to an amorphous or disordered overlayer that was thin enough to allow LEED to be sensitive to the bulk 1x1 pattern.

Silvestre and Shayegan reported direct observation of a metastable precursor for oxygen adsorption on Si(111) surfaces. This group measured time-dependent shifts in the work function of the oxygen/silicon system at low temperatures (17 K) to determine that a molecular precursor was involved in the oxidation process. They further examined the temperature dependence of this shift in time to determine the activation energy and prefactor for the conversion of this species to a stable, chemisorbed state. No indication was given, however, of specific bonding arrangements.

Umbach and coworkers then used a variety of techniques to specifically study the precursor and the stable states. Overall their findings were consistent with the previous works in that the stable state was a bridge-bonded single oxygen atom between first and second surface layers and that the precursor was in fact molecular. This group's findings did have some differences, however. Based on their experiments, they
concluded that the satellite peaks of the core-level shifts observed by others were not due to different bonding coordination numbers, but rather due to excitations. This explanation, however, seems inconsistent with the annealing behavior observed by Hollinger and Himpsel. They also concluded that the molecular precursor was most likely a bridge-bonded $O_2$ molecule (peroxy bridge) between dangling bonds on the surface. This was in contrast to electron energy loss spectroscopy (EELS) studies by Ibach and coworkers which suggested the precursor was an $O_2$ molecule bonded only at one end. Recent STM work discussed below suggests that most likely there are at least two types of chemisorbed molecular species so both studies may be consistent.

Gupta et al. used desorption studies with laser-induced thermal desorption (LITD) and temperature-programmed desorption (TPD). From these studies they concluded, like Tabe et al., that oxidation was characterized by two kinetic processes, first a fast channel and then a slow. This group also investigated the sticking coefficient, $s_o$, for $O_2$ on Si(111)-(7x7) and found that it decreased with increasing temperature. The saturation coverage (marking the slow oxygen uptake regime) was found to increase, however, with increasing temperature. They concluded that all their observations were consistent with the idea that free surface dangling bonds were required for oxidation.

At this point a fairly good picture of silicon oxidation at the molecular level was coming into focus. However, there still remained the open question of bonding configurations on the surface. Some of the first atomic-scale studies of room temperature oxidation were done on Si(111)-(7x7) surfaces. Naturally, studies with true atomic-scale
lateral resolution were only made possible with the advent of scanning tunneling microscopy in the mid 1980's. After the 7x7 reconstruction was confirmed at the atomic-scale by STM, oxidation studies soon followed. The first was done by F. M. Leibsle, A. Samsavar, and T.-C. Chiang where it was reported that the initial oxidation of Si(111)-(7x7) was essentially defect nucleated at original missing adatom defects on the starting surface. This work was followed by H. Tokumoto et al. who studied oxidation in real time and examined the relative reactivity of the Si(111) sites. They found that adatoms on the faulted side of the 7x7 reconstruction were more reactive than those on the unfaulted half, and that the center adatoms were more reactive than the corner adatoms. They also found that corner holes exhibited the lowest chemical reactivity to oxygen. In addition they concluded that [112] steps are fairly stable against oxidation.

Pelz and Koch exposed further complexity in the oxidation process by observing a previously unreported raised- or bright-adatom reacted site which was only visible with some tips and certain bias voltages. Due to this complex oxidation nature of Si(111)-(7x7), it was clear that general statements as to reactivity should be qualified by distinguishing between bright site reactivity and dark site. Furthermore, the relationship between these species also needed to be determined. By utilizing STM as well as scanning tunneling spectroscopy (STS), Pelz and Koch revealed that these sites were part of a two-stage reaction process. They found that although bright sites were present early on, subsequent O$_2$ exposure caused most of these same locations to turn into dark sites. Like Tokumoto et al., Pelz and Koch found a 4:1 preference for O$_2$ reaction with the
faulted half of the Si(111)7x7 unit cell for both types of sites. An interesting observation was that bright sites showed a 2:1 preference for corner adatom sites. Furthermore, dark sites that evolved from these bright sites also showed a 2:1 preference for corner adatom sites. However, dark sites that formed without an observed bright site "precursor" preferred center adatom locations by 2:1. Finally, Pelz and Koch found that upon thermal annealing both bright and dark sites switched to a center adatom preference.46,47

With all this varied information it is not surprising that a single set of bonding models consistent with all the techniques was yet to be agreed upon. Avouris and coworkers48,49,50 found much the same results as Pelz and Koch and have pursued understanding this process by utilizing selective chemistry with the STM tip. In a recent work51 they demonstrate the reversible conversion of bright to dark sites. After a bright site is formed it will usually turn dark upon subsequent O₂ exposure.46 Then after scanning over the area with high bias voltage, the bright site reappears.51 In addition, Avouris et al. also find doubly dark sites (2 dark sites next to each other) which can be converted into a bright site and a normal adatom site with similar electron irradiation.51 In these cases the electron energy is tuned to a transition to a dissociative state as shown in photofragmentation studies of the same O₂ precursor by Dujardin et al.53 As depicted in Fig. 1.8, Avouris et al. believe the single dark site to be a chemisorbed O₂ molecule on top of an adatom with an existing oxygen atom inserted in one of its back-bonds and that the double dark site is a bridge-bonded O₂ molecule between one rest-atom and an adjacent adatom. They claim the double dark site comes from this molecule alternating between two adjacent adatoms next to this rest-atom (Fig. 1.8).51
Recent work by Dujardin et al. correlates the saturation of bright site density with the saturating intensity of a 3.8 eV band in UPS measurements. They claim that this band corresponds to molecular oxygen absorbed on the surface and hence conclude that the bright sites are molecular in nature. This result, however, seems inconsistent with the reproducible transformation of bright to dark sites performed by Avouris and co-workers. Avouris showed that bright sites made dark with subsequent oxygen exposure could be made bright again by injecting STM current into the location (presumably to desorb a peroxy O₂ molecule as shown in Fig. 1.12). It is difficult, then, to imagine how injecting current into the site could cause the reappearance of an O₂ molecule. Clearly more work needs to be conducted in this area to determine the appropriate configurations while maintaining consistency with all the past experimental data.

1.3.2 Room Temperature Si(001)-(2x1) Oxidation

Considerably less work has been done on room temperature Si(001)-(2x1) oxidation. Cahill and Avouris demonstrated that even at room temperature some oxidation events caused the ejection of silicon dimers from the surface. They further showed that if such a surface was subsequently annealed, that these ejected dimers would coalesce to form anisotropic, epitaxial islands. As to reactivity, this group and others noted that the (2x1) reconstruction was much more resilient to oxidation than the 7x7 reconstruction. Cahill and Avouris attributed this difference to the electronic nature
of the two surfaces, similar in reasoning to why the faulted half is more reactive than the
unfaulted half of the 7x7 unit cell. The Si(111)-(7x7) surface is in general metallic in that
no large gap exists around the fermi energy, while the Si(001)-(2x1) surface does have a
pronounced gap around $E_F$.\textsuperscript{62} Hamers et al.\textsuperscript{32} showed that c-type defects on the 2x1
surface did, however, have a metallic I-V response, and it was in fact found that these
defects served as nucleation points for the initial stages of Si(001)-(2x1) oxidation.\textsuperscript{58,60}
Udagawa et al. point out that the metallic nature of the c-type defect implies that they
probably have a small work function, and hence O$_2$ molecules may more efficiently
dissociate there and absorb atomically.\textsuperscript{60}

As with Si(111) the actual bonding configurations are extremely difficult to
ascertain. Kliese et al. used a fast STM to obtain sequences of the initial stages of
Si(001)-(2x1) oxidation,\textsuperscript{59} and identified a small protruding species that was only visible
at negative sample bias (imaging filled states) which they believed to be a bridge-bonded
oxygen atom between dimer rows. This type of species had also been postulated in
theoretical calculations by Zheng and Smith.\textsuperscript{55} Zheng and Smith also calculated that
oxidation should initially proceed through a molecular precursor in a bridge-bonded site
followed by a rapid dissociation into atomic oxygen species in the "long" bridge site
between dimer rows and the other oxygen atom in the "short" bridge site in the adjacent
dimer.\textsuperscript{55} No evidence was found for bridging sites between dimers within a given row.\textsuperscript{55}

Another feature observed by the STM studies\textsuperscript{58,59,60} was that dimers that originally
appeared symmetric buckled after a local oxidation event. This buckling was observed to
oscillate from dimer to dimer as is commonly observed around the c-type defect.\textsuperscript{32} It is
believed that it is the asymmetric nature of the defect or, in this case the asymmetry of the adsorbed oxygen configuration, which induces this buckled pattern. The buckling is observed most strongly adjacent to the defect then dies away with increasing distance from the reacted site.

1.3.3 Critical Conditions for Silicon Oxidation

At elevated temperatures, another aspect of silicon oxidation must be considered. It is well known that exposing Si to O$_2$ can, depending on substrate temperature $T_s$ and oxygen pressure $P_{ox}$, either form a solid oxide film or etch the surface (via the evolution of volatile SiO). The net chemical reactions are shown below.

$$O_2(g) + Si(s) \rightarrow SiO_2(s) \quad [\text{nucleation reaction }]$$
$$O_2(g) + 2Si(s) \rightarrow 2SiO(g) \quad [\text{etching reaction }]$$

Figure 1.9 shows a phase diagram with "critical curves" as determined by Smith and Ghidini (dashed line) and Lander and Morrison (solid line). These curves separate the pressure-temperature conditions for which a clean, etched surface results (the so-called active oxidation regime) from those in which a SiO$_2$ film will result (the passive oxidation regime). When evaluating any study of silicon oxidation it is important to consider which portion of this diagram the experiments are done in, as well as the proximity to the critical curves.
One variable missing from this phase picture, however, is time. Both Lander and Morrison and Smith and Ghidini did not specify total exposures in their determinations. Lander and Morrison increased the $O_2$ partial pressure while holding the sample at an elevated temperature and waited for LEED to show "a large reduction in pattern intensity in a reasonable time (not too many hours)…" to conclude that the surface was oxidized. Smith and Ghidini used optical pyrometry at a fixed oxygen partial pressure to determine the sharp, visible boundary on a silicon sample that had a temperature gradient established across it. Simultaneously, the temperature at which the boundary occurs could also be determined, but the exposure times were again not specified very well. An accurate determination of whether the surface is oxidized or etched should include mention of the total exposure (or dose) used to make the determination. It should be noted, however, that the critical conditions determined by both groups were linearly consistent with one another as can be seen in Fig 1.9. In addition, the conditions were found to be independent of crystal orientation as well as doping.

Of particular interest is the area in P-T space right around the critical line, i.e. the "transition region" between active and passive oxidation. At high temperatures (> 1000°C), μm-sized "growth" features were observed at high doses within this narrow transition region. It was postulated that these features were SiO$_2$ coated silicon pyramids which started as small patches of oxide that nucleated during the initial stages of oxidation. It was believed that these patches (or "oxide clusters") grew laterally as the surrounding clean silicon was etched away, thereby coating the sides of an etched
pyramid (Fig. 1.10).\textsuperscript{65} Even at lower temperatures it was believed that a roughening mechanism existed within this transition regime which lowered breakdown voltages in devices that were made with processing conditions that crossed the critical line.\textsuperscript{69} The specific roughness was never quantified, however, and was not related to the large etch features seen at higher temperatures.

Lutz et al.\textsuperscript{67} used UPS and XPS in this transition regime on Si(001)-(2x1) to determine that at high temperatures (> 600°C) and low oxidation pressures the surface was a combination of SiO\textsubscript{2}-like regions (Si bound to four O atoms) and bare silicon. In contrast, they found that room temperature oxidation could be explained with a random distribution of oxygen in intermediate bonding configurations. Tabe et al. also provided evidence for phase separation of oxidized areas of silicon and clean silicon using AES, LEED, and UPS after oxidizing at elevated temperatures.\textsuperscript{39} It will be shown that these findings are quite consistent with the oxidation behavior observed in this work. Furthermore, it will be the focus of this work to concentrate on the atomic-scale evolution of silicon surfaces within this transition regime in hopes of identifying mechanisms for oxidation in this lower temperature (< 800°C) regime which is increasingly important to modern semiconductor processing.

1.3.4 Elevated Temperature Si(111)-(7x7) Oxidation

Among the early studies of elevated temperature oxidation were the modulated molecular and atomic beam methods of Memmert and Yu\textsuperscript{72} and Engstrom et al.\textsuperscript{73} One
issue addressed was the sticking or reaction coefficient, $s_0$, of oxygen on silicon. Memmert and Yu studied both the Si(001) and Si(111) surfaces and found that for incident $O_2$ energies $< 0.08$ eV the reaction coefficient was correlated with the number of dangling bonds on the surface. The coefficients found were 0.055, 0.08, and 0.1 for Si(111)-(7x7), Si(001)-(2x1), and Si(111)-(1x1) respectively. For incident energies greater than 0.08 eV they found an activated adsorption which was essentially independent of the particular surface reconstruction. A kinetic analysis of the SiO peak via time resolved mass spectrometry showed an activated process with two rate coefficients. The first rate was that to form the SiO complex on the surface after adsorption and the second was the actual desorption of this complex as a volatile SiO species. The activation energy for the formation of the species was found to be $3.0 \pm 0.2$ eV and $2.7 \pm 0.15$ eV for Si(001) and Si(111) respectively. Similarly, the activation energy for desorption was found to be $4.0 \pm 0.37$ eV and $4.4 \pm 0.15$ eV on the two surfaces.

Engstrom et al. used modulated molecular beam reactive scattering (MMBRS), XPS, and TPD to perform similar studies on both Si(001) and Si(111). They found that at high temperatures (using an atomic beam of oxygen) a stable surface intermediate was formed which was believed to be either an isolated oxygen adatom or an adsorbed SiO complex. They also found that if a molecular oxygen beam was used, a precursor peroxy radical or peroxide bridge was involved, consistent with the work presented above. They postulated this precursor would dissociate to form the same stable surface
intermediate as with the atomic beam. The rate coefficients for these processes were derived from an analysis of the SiO product waveforms obtained from time-of-flight mass spectrometry. For the atomic beam a single first order rate was consistent with the SiO waveform while with the molecular beam, the time dependence was consistent with a combination of two first order rates as \( \exp(-k_2t) - \exp(-k_1t) \) with the second rate yielding the same coefficient as that with the atomic oxygen. Thus Engstrom et al. concluded net reactions as follows:

\[
\begin{align*}
\text{O}(g) + \text{Si}(s) &\rightarrow I' \rightarrow \text{SiO}(g) \\
\text{O}_2(g) + \text{Si}(s) &\rightarrow I_1 \rightarrow I_2 \rightarrow \text{SiO}(g) \quad \text{with } I' = I_2.
\end{align*}
\]

A more detailed discussion of subsequent modeling deduced from this study will be presented in the discussion of this manuscript. It will be shown that the model deduced from this spatially averaging surface technique is consistent with the data presented here based on an analysis of nanometer-scale oxide cluster nucleation and growth.

Using transmission electron microscopy (TEM), Ross and Gibson were able to watch the evolution of the Si/SiO\(_2\) interface during oxidation. In particular they observed the lack of step motion during passive oxidation and terrace intensity fluctuations that were consistent with a layer-by-layer growth mode. In active oxidation they found that oxygen again reacted on terraces, but now saw significant step motion. They attributed this motion to the preferential desorption of SiO from step edges, but provided no evidence that this was in fact the case. In the light of more recent STM studies, this behavior is explained better with a mobile vacancy theory in which random SiO
desorption can occur from terraces as well as possibly from steps. Although direct evidence for desorption of SiO from step edges is difficult to show, the presence of monolayer deep holes (coalesced vacancies in a terrace interior) suggests that there is at least desorption from interior terrace sites.

In a later study this same group also examined temperature-pressure conditions within the transition or “roughening” regime. They noted that this regime was marked by the competition of stable oxide formation and oxidation-induced etching. They used the term “micromasking” to refer to small nucleated oxide clusters that prevented the underlying silicon from etching. It will be shown below that the work presented here shows the most conclusive evidence yet of this micromasking mechanism and begins to quantify the evolution of surface morphology within this regime.

The first STM study of active Si(111) oxidation was done by Feltz, Memmert, and Behm. Like Ross and Gibson, they too observed a step-flow mechanism but only for removal of the top 7x7 layer. Subsequent etching proceeded through the nucleation of pits on freshly exposed surface layers. They attributed this behavior to the fact that the freshly exposed layer, although 7x7 reconstructed, was highly defective with many grain boundaries and regions of imperfect 7x7. In both cases, however, the etching was attributed to the diffusion of adparticles (either oxygen or a surface vacancy) that terminate at step edges or pit edges around defects in the new surface layer. They found that once a monolayer was removed all subsequent etching was via pit nucleation and growth; typically 3 layers were exposed at a time.
In some cases this group also observed the pinning of step edges during the first monolayer removal which was attributed to surface defects. These defects were subsequently identified by Doing et al. as oxide nuclei. They found that once a step was pinned, a long “finger” would form which would subsequently have its base etched away leaving a monolayer high island on the surface. They also found that the shape of these fingers was dependent on the temperature at which the oxidation was done. At 637°C the fingers were dendritic, at 697°C the steps were faceted, and above 727°C the fingers were rounded. The behavior observed is consistent with the work presented here which focuses on the same finger-like formation of step structures on Si(001). A more detailed discussion of this group’s most recent work will be incorporated into the discussion.

Shortly after these studies Ono, Tabe, and Kageshima came out with a study of oxidation at 600°C using STM and XPS. Similar to room temperature results they found increasing areas of dark regions on the surface which scaled with the oxygen coverage obtained from XPS measurements. At elevated temperatures they noted these dark areas were clustered together while at room temperature they remained random even at the atomic level. One interesting addition this study made was that the depth of the dark areas was very much bias dependent consistent with the electronic reduction of the density of states at the Fermi level expected from oxidation. In addition they found that at higher temperatures the dark areas were darker than at room temperature which the authors believed indicated a greater depth for the oxidation as based on their tight binding calculations.
1.3.5 Elevated Temperature Si(001)-(2x1) Oxidation

Like the oxidation of Si(111), Si(001) oxidation has been studied extensively at high temperatures, especially recently. One of the earliest studies by D’Evelyn, Nelson, and Engel used molecular beam, XPS, and ion scattering spectroscopy (ISS) to examine oxidation kinetics and sticking coefficients. Their findings were generally consistent with the later work of Engstom et al. on both silicon surfaces. The initial sticking coefficient was found to decrease with increasing temperature up to 127°C, but was found to increase with increasing temperature above 327°C (presumably an enhanced activated adsorption). For transition regime oxidation, this group concluded that oxide nuclei grow as islands while the etching of silicon between these islands continues. This conclusion, although not observed directly, was inferred from modulated molecular beam experiments where the SiO signature was again monitored to find that even at a coverage of 2.8 ML the magnitude of SiO signal was still 28% of its value on the clean surface. This indicated that the corresponding fraction of the surface is clean and the rest of the oxide is segregated into islands. Later the same group continued these experiments and extended investigation to include the Si(111) surface as mentioned previously, and eventually employed the use of STM to investigate oxide decomposition and void formation.

Another molecular beam method was used by Yu and Eldridge to determine similar kinetic information as that obtained in this group’s study of Si(111). The
signature of the SiO peak again implied a difference of two activated processes implying a surface intermediate to desorption. The rate to form the desorption precursor had an activation energy of 2.5 eV and for this species to actually desorb, an activation energy of 3.0 eV was found.\textsuperscript{81} In contrast, it should be noted that their later work (mentioned above) found a desorption rate given by a 4.0 eV activation energy.\textsuperscript{72}

Kahata and Yagi used reflection electron microscopy to investigate the diffusion of oxidation-induced vacancies on Si(001)-(2x1).\textsuperscript{82} They showed that during oxidation at $10^{-8}$ torr and 700°C vacancy islands formed only on the A-type terrace. This observation was attributed to the fact that the density of vacancies must be on average greater on these terraces than on B-type terraces. The conclusion reached was that diffusion of vacancies must be highly anisotropic such that their lifetimes on A terraces were longer than on B terraces.\textsuperscript{82}

Similar anisotropic vacancy island nucleation was observed by Bedrossian and Klitsner from sputter-induced vacancies created on Si(001).\textsuperscript{83,84} They determined that the vacancies preferentially terminated at B-type step edges causing their preferential retraction. They showed that 0.5 ML removal caused almost the complete retraction of the B-type step leading to the creation of single domain structure.\textsuperscript{84} This structure could be beneficial in subsequent epitaxial growth of III-IV GaAs in that it would avoid anti-phase boundaries in the resulting epitaxial layers. The work of Kahata and Yagi and Bedrossian and Klitsner suggests that with a low density of oxidation-induced vacancies at high temperatures, a single domain structure may also be created without resorting to mechanical sputtering. Oxidation-induced etching could be a potentially beneficial
process in industry since it might be a cost effective way of producing single domains or other etch structures.

Some of the first atomic-scale studies of elevated temperature Si(001) oxidation were done by Udagawa, Niwa, and Sumita. This group used STM to investigate the initial stages of oxidation at 600°C. Their work revealed Si islands along with oxidized regions that appeared as dark sites, as sequences of dots, and as dots with dark surroundings. With the flux turned off, and the temperature maintained at 600°C most of the dark sites disappeared, but the dots remained. Further annealing to 800°C removed all evidence of the oxides. These authors concluded that the dots were sequences of Si atoms stabilized between oxygen atoms (in between dimer rows) and claimed them to be the first atomic-scale evidence of a thermal oxide.

In addition to our work presented here, some concurrent work on Si(001) was independently published by Tsong and coworkers and will be addressed in detail during the discussion of the present work since there is substantial overlap in content.

1.3.6 Summary of Key Oxidation Results and Outstanding Questions

A summary of the key points which are generally agreed upon about silicon oxidation are listed below:

- oxygen can either nucleate a stable oxide film or etch the surface depending on the silicon substrate temperature and oxidation pressure.
• the initial stages of silicon oxidation follow at least a two stage process with molecular chemisorption followed by dissociation and then insertion of atomic species into bridge- or back- bonds.

• macroscopic, averaging techniques have been used to identify the existence of an oxidation precursor and a precursor has also been established for oxidation-induced etching.

• oxide clusters can pin retracting steps during oxidation-induced etching.

• roughening occurs in the transition regime which degrades the performance of devices fabricated with oxidation conditions within this regime.

• some oxidized sites appear to be unstable at elevated temperatures.

Despite the extensive study of the initial oxidation of silicon just presented, the fundamental atomic-scale mechanisms underlying sub-monolayer oxide nucleation and growth are still not well established. A number of atomic-scale models have been proposed and compared with macroscopic measurements of Si surface oxidation over a range of temperatures and oxidation pressures, but to date little has been done to directly compare microscopic predictions of these models with microscopic measurements of oxide nucleation and growth kinetics. Such a direct comparison would be an important test of the validity of competing atomic-scale models.

In addition, the boundaries of the transition regime should be quantified especially at lower temperatures. Since many Si processing steps involve transient, low-temperature
exposure to background levels of O₂ and H₂O, a knowledge of the conditions which produce surface roughening and a characterization of the roughness thus produced has great practical importance.⁶,⁷,⁸,⁹,¹⁰

The outstanding questions that remain are then:

- what are the atomic-scale mechanisms involved in initial silicon oxidation?
- what are the true boundaries of the transition regime in temperature-pressure space?
- how does surface morphology evolve as functions of temperature, pressure, and dose within the transition regime?
- what is the source of roughening in the transition regime, and because of its great practical importance in device performance, can we quantify it?
- can discreet nanometer-sized oxide islands be imaged with STM?
- at which point does oxide growth crossover from oxide island nucleation to monolayer-by-monolayer oxide growth?
- can atomic-scale models and the corresponding oxidation kinetics be directly tested by analyzing STM data?
- can oxidation-induced surface etching be utilized in microprocessing the silicon surface, and can we control the nucleation and growth of oxide clusters?
Hopefully by addressing these questions, this manuscript will be able to add to the current understanding of oxide nucleation and growth and oxidation-induced etching on silicon surfaces. As mentioned in section 1.1, this understanding of fundamental kinetic processes underlying silicon oxidation may one day be useful in tailoring integrated circuit processing to meet the industrial need for a thin, reliable transistor dielectric or other possible applications yet to be conceived.
Figure 1.1 Crystal structure of silicon. (a) unit cell of bulk silicon [from Ref. 4]. The structure is face centered cubic with a basis of two. (b) coordinate reference frame. (c) Crystalline planes as defined by Miller indices [from Ref. 17].
Miscut = $\tan^{-1}(\text{step height} / \text{average terrace width})$

\[\tan^{-1}(1.358/300) = 0.26^\circ\]  \hspace{1cm} \text{(a)}

\[\tan^{-1}(3.135/300) = 0.60^\circ\]  \hspace{1cm} \text{(b)}

Figure 1.2 Miscut on vicinal silicon surfaces. (a) Calculation of miscut for Si(100). (b) Calculation of miscut for Si(111).
Figure 1.3 Si(100)-(2x1) reconstruction. (a) Ball-and-Stick model for the ideally bulk terminated and reconstructed surfaces. (b) 92 Å x 77 Å STM image of the reconstructed surface. Individual dimers are boxed. Buckled dimers are shown in dashed box. Arrows indicate dimer row direction. (c) Model of dimer buckling.
Figure 1.4 Si(100)-(2x1) surface steps. (a) ball-and-stick schematic of the $S_B$ step with dimer rows on the upper terrace perpendicular to the step direction and the $S_A$ step with the dimer rows on the upper terrace parallel to the step direction [after Ref. 18]. (b) STM greyscale images showing rough (wavy) B-type steps and smooth (straight) A-type steps.
Figure 1.5 Atomic-scale defects on Si(100)-(2x1). (a) A, B, and C-type defects [after Ref. 32]. An A-type defect is believed to be a complete missing dimer, a B-type to be two adjacent missing dimers, and the C-type to be two adjacent half-missing dimers. (b) Antiphase boundary where dimer rows on the same terrace are discontinuous and shifted by one half a row across the boundary.
Figure 1.6 Dimer-Adatom-Stacking (DAS) fault models for Si(111) surfaces [from Ref. 33]. The original DAS model for the 7x7 reconstruction was first determined by Takayanagi [Ref. 34]. The 7x7 is the lowest energy reconstruction while the 5x5 and 9x9 reconstructions are metastable.
Figure 1.7 Si(111)-(7x7). (a) STM image of Si(111)-(7x7) with superposed DAS model overlay. Image size is 74 Å x 71 Å. Arrow indicates a missing adatom defect. White atoms in the overlay correspond to the adatoms observed in STM images. (b) Sideview of DAS structure [after Ref. 34].
Figure 1.8 Possible oxygen bonding configurations. (a) Density of States as a function of energy for oxygen atoms in various bonding configurations [from Ref. 49]. (b) Bonding sites and conversions as suggested in Ref. 51.
Figure 1.9 Critical conditions for the oxidation reactions. The dashed line is from Ref. 65 and the solid line is from Ref. 63. These lines represent the critical conditions which separate the region of pressure/temperature space where an oxide film will eventually form from the region which will be left free of oxide due to volatile SiO desorption. The slope of these lines implies an activation energy for SiO desorption of roughly $3.3 \text{ eV}$. 
Figure 1.10 Schematic of nano-masking. As the surface layer is being etched downward, the oxide cluster is growing in size laterally and thus protecting or masking the underlying silicon from etching. [after Ref. 65] Large etch features are created by this mechanism in the transition or roughening regime.
CHAPTER 2

EXPERIMENTS

2.1 Overview of Experiments

We have used scanning tunneling microscopy (STM) to study the atomic-scale effects of oxidation on Si(111)-(7x7) and Si(001)-(2x1) surfaces as functions of temperature, pressure, and dose. Silicon substrate temperatures, \( T_s \), have ranged from room temperature to 940°C with most experiments centered in the 640 - 740°C range. Oxidation pressures, \( P_{ox} \), have ranged from 1x10^{-6} torr to 4x10^{-6} torr, and doses, \( D_{ox} \), have been extended as high as 2000 L where 1 L (Langmuir) is defined as an exposure at 1x10^{-6} torr for one second. Additional variables that were considered include starting surface defect density, doping, and vicinal surface miscuts (ranging from <0.1° to 3.0°).

A major observation on both silicon surfaces is that oxygen-induced etching of the surface becomes an important process for low O\(_2\) pressures (\(~ 10^{-4}\) torr) at temperatures greater than about 540°C. This etching leads to the creation of mobile vacancies which can diffuse across the surface, coalesce to form monolayer-deep depressions, or terminate at
steps causing them to retract. This behavior is similar to that observed for vacancies created by sputter-ion etching of silicon at similar temperatures.

An original finding on Si(111)-(7x7) is that newly exposed surfaces near retracted steps are often observed to reconstruct into metastable 5x5 or (occasionally) 9x9 structures, as well as the stable 7x7 structure. On Si(001)-(2x1) oxidation-induced vacancies were found to preferentially terminate at B-type step edges causing their retraction and the corresponding reduction of B-type terraces. Theoretically, as exposure is increased this should tend to create single A-domain structures. However, the creation of a single domain surface was interrupted by step pinning.

At higher doses (and present on both crystalline planes) this pinning causes the formation of multi-layer Si islands and long fingers extending from surface step edges. High resolution images indicate that pinning is caused by nm-scale oxidized regions which resist the etching process. By counting the pinning sites, and correlating each site to a single oxide nuclei, we have made the first direct estimates of the oxide cluster nucleation rate $J_\alpha$ and its dependence on pressure, temperature, and dose. We find that $J_\alpha \propto P_\alpha^m$, where $m \geq 2$, consistent with a model in which two diffusing oxygen surface species are required to nucleate a stable oxide cluster. In addition, we find that (1) the initial oxide cluster nucleation rate is related to a sum of individually thermally activated processes which have an effective activation energy in the range -3.3 to -4.0 eV, (2) oxide nucleation is strongly suppressed at high $O_2$ doses ($D_\alpha > \sim 200$ L), even though the $O_2$ coverage remains much less than one monolayer, and (3) the vertical surface etch rate $\eta$
at locations *between* nucleation sites remains roughly constant. Taken together, these observations impose rather restrictive constraints on possible atomistic models. We have used rate equation analysis and Monte Carlo simulations to check different models, and find that a single "oxide-species" diffusional model is insufficient to account for both suppressed nucleation and constant etching, while a dual-species diffusional model (such as that proposed by Engstrom *et al.*[73]) is consistent with the observed data. This provides the first direct *atomic-scale* support for such a dual-species model.

We have also used STM to study the roughening of Si(001) surfaces produced in the low temperature roughening regime. At low O$_2$ doses ($D_{\text{ox}} \leq 50$ L), the roughness is in the form of Si fingers and small islands (presumably oxygen capped Si islands). At higher doses, however, these pinning sites lead to the creation of three-dimensional conical "island" structures as prolonged surface etching removes the surrounding material. These structures may be early stages of the μm-sized "growth" features observed by Smith and Ghidini at higher temperatures, pressures, and doses.[65,66] At $T_s \equiv 640^\circ\text{C}$ and $P_{\text{ox}} \equiv 6 \times 10^{-4}$ torr, the average island height and rms surface roughness were found to scale approximately linearly with dose. The surface etching was directly determined from the dependence of island height vs. dose, which indicated a sticking coefficient $s_p \equiv 0.04$ (±0.02) for O$_2$ on Si under these conditions. Finally, we have started to delineate the boundaries in temperature-pressure space that result in significant atomic-scale surface roughening, and have found them to extend to pressures several orders of magnitude above the commonly accepted critical line for net SiO$_2$ growth.
2.2 Scanning Tunneling Microscopy

2.2.1 Fundamental Principles

Many excellent reviews of scanning tunneling microscopy are available,\textsuperscript{95,96,97} so only a brief overview of the technique will be presented here. The underlying principle to STM is that if two conducting materials are brought close enough together, electrons will be able to quantum mechanically tunnel from filled states in one material to empty electronic states at the same energy in the other (Fig. 2.1). In addition to the availability of states, quantum theory shows that the tunnel current that flows between the materials is exponentially dependent on their separation. The idea then is to bring a sharp metallic tip close to a relatively flat sample, establish a bias voltage between them, and allow a tunnel current to continuously flow as the tip is raster-scanned across the sample. In the most common mode of operation, an electronic feedback loop measures this current and continuously adjusts the height of the tip over the sample in order to keep the tunnel current constant. A schematic overview is shown in Fig. 2.2.

Since the tunnel current is exponentially dependent on the separation, only a few atoms at the end of the tip will contribute to the tunnel current. This allows for a high spatial resolution, and changes in the current can be attributed to localized changes in electronic density on the surface. It is important to note that the changes in electronic density can have two different origins. The first is that some features on the surface may actually be topologically higher than others, and hence current would tend to increase...
over these regions, so the tip must rise to keep the current constant. The second is that there may be electronic fluctuations in the local density of states (LDOS) on the surface which can either increase or decrease the available states for tunneling, so the tip may rise over these locations or push down into them (Fig 2.2). The information that is actually obtained from the microscope is this relative height of the tip as it is raster-scanned across the surface. The data are usually displayed in a greyscale image where bright is a high tip position and dark is a lower tip position. This type of image is called a constant current topograph and is often considered to be a “map” of constant electronic state density on the surface being examined. This constant state density is actually the integrated state density from the Fermi level to the applied bias voltage.

2.2.2 Interpretation of STM data

As stated in the previous section, bright and dark features on an STM scan must be deconvoluted to determine which is topographical in nature and which is electronic. Without previous knowledge of what the surface “should” look like, this can sometimes be a difficult task. One way to discern between “true height” and “electronic height” is to change the bias voltage and scan the same area. In doing so, the energy of the tunneling electrons is changed. With electronic defects, the profile of the local density of states as a function of energy is often different than profile for the surrounding material. Therefore, changing the energy of the tunneling electrons may increase or decrease the relative height of an electronic feature with respect to the surrounding material. On the other
hand, if the feature is a truly topographic in nature, then the electronic density of states is often the same (as in the case of an atomic step) for the feature and the surrounding area so no relative change in apparent height (or depth) is found.

Another important consideration is the direction of the tunnel current. At positive sample bias, electrons are moving from filled tip states to empty states in the sample. A scan taken under these conditions would be considered an empty state image. Conversely, at negative sample bias the tip is probing filled states in the sample. At the atomic level on silicon, there is generally an increase in the electronic density (both filled and empty states) centered over each adatom of the 7x7 reconstruction. This being the case it is generally possible to obtain atomic resolution on Si(111)-(7x7) with the adatoms appearing bright at both biases (recall the adatoms are topographically higher as well). At positive sample bias the unit cell looks symmetric, but at negative sample bias the faulted half of the unit cell appears brighter purely from electronic considerations since it can be seen from Fig. 1.7 (b) that topographically both halves of the 7x7 unit cell are at the same height.

On the 2x1 surface, the filled electronic density is located between the atomic positions in the covalent dimer bond. This being the case, at negative sample biases, the dimer bonds appear bright, and rows of dimers are seen as shown in Fig. 1.3. At positive sample biases, it turns out that the empty states are more localized over the atomic positions of the dimer and are thus separated. With a particularly good tip then, an empty state image can often resolve "single atoms" on the 2x1 surface.
With chemical reactions, distinguishing between electronic and topographical effects can be even more difficult. In the case of oxygen exposure, the electronegativity of oxygen tends to increase the localized electronic charge around the oxygen atom. In general, calculations are needed to predict what the new LDOS will look like after a reaction (Fig 1.8). The geometrical configuration must also be included in these calculations. As was mentioned in the review of silicon oxidation, it is this type of calculation with corresponding STM data that has helped researchers try to identify the possible atomic configurations occurring after oxidation on Si(111)-(7x7) surfaces (Fig. 1.8).

A related technique which tries to probe these electronic changes is called scanning tunneling spectroscopy (STS). This method is similar to STM, but at various points throughout a scan the feedback controller is disabled, and the bias voltage is ramped. Here, the tunnel current is directly measured and (dI/dV)/(I/V) is plotted versus voltage. This curve is a good approximation to the form of the LDOS over that point. The largest difficulty with this technique is that complications may arise from a non-uniform density of states for the tip. Often the tip is accidentally (or intentionally) crashed at which point the elemental nature of the tip becomes unknown. In addition, such a crash may change the shape of the tip and thus also alter its electronic state configuration. After this occurrence it is difficult to tell anything absolutely about the sample’s LDOS, but provided the tip is at least stable (and not crashed) through subsequent scans, relative changes in I-V response can be attributed to electronic differences on the sample, and site distinctions may be obtained.
2.2.3 Apparatus

The STM was first developed by Binnig and Rohrer in 1982. In 1986 they were awarded the Nobel prize for their discovery. A schematic of their early design is shown in Fig. 2.3. The two primary parts of the microscope are the walker and the scanner. The walker is used to position the tip and sample to within nanometer proximity to one another. The scanner is then used to raster scan either the tip or the sample to acquire the image. Scans sizes range from a few Angstroms on a side on up to many microns. The material that makes these atomic-scale movements possible is a piezoelectric ceramic material called PZT, lead zirconate titanate. This material will expand and contract at the atomic-scale in response to an electric field. The intrinsic gain of common walkers or scanners used today is generally 10's of Angstroms per volt applied.

The STM used in these experiments has been described briefly elsewhere, but will be described in detail here. The specific design of the walker used for these experiments is a Besocke type walker. This is a form of inertial walker which consists of three, sapphire-capped piezo tubes which have nickel electrodes that are sectioned into quadrants (Fig. 2.4). A sample stage simply sits on the caps of these tubes and is inertially slid forwards, backwards, and to either side by bending the piezos in the desired direction, then rapidly resetting their position. The voltages which cause the tubes to bend are applied via the electrodes as shown in Fig. 2.4(b). It should be noted that with
these quadrant-type tubes, the piezo material primarily expands and contracts in a direction normal to the direction of the applied field with only small distortions in the direction parallel to the applied field (due to a small, non-zero Poisson's ratio). Descriptions of other types of walkers are addressed in the previously mentioned reviews of STM. 95,96,97

The scanning mechanism of this particular microscope consists of a piezo cross (as shown in Fig. 2.5(a)) to achieve x- and z-motion and a piezo tube (similar to that shown in Fig. 2.5(b) but with a single outer electrode) mounted in the center of the cross to achieve the y-motion. Note that a general convention in STM is to have the tip-sample separation axis be defined as the z-direction. In normal operation, x- is the fast scan direction and y- is the slow scan direction. A particular disadvantage to this type of design is that it is very difficult to achieve perfect orthogonality between the x- and y-directions. A more conventional design uses a tube scanner in which all three coordinate motions come from the same tube (Fig. 2.4(b)).

To achieve the longest time possible for useful data acquisition between UHV pump-downs, a tip mount was designed that could hold many tips at a time. A picture of this tip mount is shown in Fig. 2.5(c). The holder is made out of Invar (magnetic) and sits on top of a circular, neodymium-iron-boron magnet that is mounted at the top of the y-scanner tube. This “carousel” design allows for a post to come down (in situ) between the tips (which flair out like spokes from a wheel) and rotate the mount around to choose the desired tip. In this way, six tips may be successful used without bringing the entire system up to atmosphere.
Some flexibility also exists for the samples. This microscope is designed to accommodate two samples at a time. The sample stage (Fig. 2.6) is constructed out of Macor ceramic and a quartz base to allow for easy slip on the Besocke walker. The actual samples are held in place between Ta wings (which make contact with the heating stage) and Mo clips (Fig 2.6). In addition, silicon buffer pads are used to further isolate the sample's surface from coming in contact with the metal clips which is especially important during high temperature processing steps which can cause metallic contamination to diffuse across the sample. The stage is mounted at the end of a rod attached to an ex-situ rotateable, x-y-z translator.

The scanner and walker are mounted on a large piece of Macor for electronic insulation which is weighed down with a large piece of stainless to steel. This assembly is then suspended from 4 Viton O-rings (for vibration isolation) which are attached to rods extending to a 6” base flange. Half way up the rods which suspend the scanner unit is a high temperature heating stage which has thick (~2 mm diameter) copper wires attached to it so that as much as 12 -15 amps of current can be passed through the samples. A picture of the entire microscope is shown in Fig. 2.7.

In addition to the 4 O-rings, vibration isolation also comes from using thin, 3 mil wires to make all electrical connections from the base flange to the microscope. The wires are coated with a UHV insulation from California Fine Wire Company. Additional vibration isolation comes from a Newport air table which suspends the entire UHV system. For most scans the o-ring isolation by itself was sufficient, and the air table was rarely raised. Another measure taken to ensure good vibration isolation is to fully
decouple the sample stage's hooks from the manipulator's hooks. Finally the entire laboratory is located in the basement which helps reduce building vibrations from affecting the scans.

2.2.4 STM Electronics

For a theoretical treatment of control electronics, the interested reader is referred to one of the general STM references listed previously. Presented below is a brief, qualitative overview of the most important electronic components.

Walker control electronics

Originally the Besocke walker was controlled with waveforms generated from Quatech WSB-10 boards in the computer. This turned out to be somewhat inconvenient in that every time the sample needed to be moved, the STM scanning program would have to be exited and the "walker program" had to be initialized. To facilitate the process (and free-up expansion slots in the computer), an external box of electronics was designed which could reproduce the waveforms and hence move the sample without using the computer. The waveforms which are sent to the tubes have a sawtooth shape where both amplitude and frequency can be adjusted for optimal motion. In addition, the box was designed to be addressed by the General Purpose Interface Bus (GPIB), so that an automated sample/tip approach routine could be utilized. This program was written by V. Brichzin and works as follows: the tip is retracted, a couple of steps are taken, the tip
is probed forward, and the presence of tunnel current is checked for. The cycle is repeated until tunnel current is found. This process decreases the chance for an accidental crash as compared to the same procedure when done manually.

**Tip Preamplifier**

Typical tunnel currents used during STM imaging of a sample are on the order of one nanoamp (1 nA). Currents this small are extremely susceptible to noise from various sources and hence it is desirable to amplify this current as close to its source (the tip-sample tunnel junction) as possible. Since the junction is in a UHV environment, a current amplifier is placed just on top of the 6” base flange. This amplifier has a fixed gain of $10^8$ V/A. Thus 1 nA of tunnel current results in 100 mV being input to the feedback control unit.

**Feedback Control Unit (FCU)**

At the heart of the STM electronics is the feedback control unit (FCU). This unit compares the incoming tunnel current (a voltage after the tip preamplifier) with the current requested (externally) by the operator and any difference is translated into a voltage that is sent to the FCU’s output ports. This is the voltage that is required to move the z-piezo closer or further away from the sample in order to keep the tunnel current matched to the constant current requested. This voltage is of course sent to the z-piezo so the tip’s height is actually changed, and it is also sent to the computer where it is digitized and recorded as the primary data.
There are many different designs for the FCU which will accomplish the desired tracking of the tip across the sample. For a detailed discussion of these control circuits, the interested reader should see S. Park's and R. Barrett's theoretical discussion of STM design considerations in Scanning Tunneling Microscopy. A brief summary of their findings are reported below.

There are three basic components that can be incorporated into the FCU to determine how the output voltage will be calculated. These are proportional, integral, or differential feedback control circuits. The proportional is the only control component used in these experiments, but for completeness the others will be presented as well.

The response function, $G(s)$, of a feedback loop is the Laplace transform of the input function, $f(t)$:

$$G(s) = \int f(t)e^{-st}dt$$

with the generalized types of response functions being:

$$G(s) = A \frac{\omega_c}{s + \omega_c}$$ for proportional response

$$G(s) = \frac{A}{s}$$ for integral response

$$G(s) = A\omega_c \frac{s}{s + \omega_c}$$ for differential response

where $A$ is the gain and $\omega_c$ is the cutoff frequency.

In general, the user desires the control circuit's response to be as fast as possible while still maintaining stability and negative feedback. For the proportional response
function, both a gain and a cutoff frequency are externally set by the user. Figure 2.8(a) shows the calculated response of a proportional circuit to a step function with different combinations of gains and cutoffs. It should be noted that the faster the response, the greater the oscillation. It should also be noted that with this method there is a steady state error signal, which is just the difference between the measured tunnel current and the set-point current as defined by the user. Fortunately, this constant offset in the error signal is not much of a concern unless accurate measurement of the tunnel current is necessary.

For an integral circuit (Fig. 2.8(b)), only a gain is set. Here it can be seen that although the response time is somewhat slower than that of the proportional circuit, the steady state offset is removed. Again, the higher the gain, the more oscillations that appear in the response function.

Finally, if the fastest response possible is desired (e.g. for fast scanning of rough surfaces with high frequency corrugation), the combination of a differential plus an integral control circuit is the optimal configuration. As can be seen in Fig. 2.8 (c), this combination will most accurately reproduce the step function, provided that some large amplitude oscillations at the edges can be tolerated. This larger instability is the price that is paid for the faster transient response. To conclude, then, the type of control circuit used should be chosen based on the type of samples one is looking at, as well as the type of information desired. There is always a trade-off of response time and stability. For this study, a high speed scan rate was not required and current offsets were not a concern, so the reasonably fast and stable proportional system was used.
In addition to oscillations from the feedback loop, mechanical vibrations may also be present which can similarly introduce noise into the data. Mechanical vibration must be dealt with by using vibration isolation techniques listed above (e.g. o-ring suspension of heavy STM stage, air table isolation for entire UHV system, small wire coupling of STM to outside environment). Provided their amplitude is not too large, mechanical vibrations or electronic oscillations can be present during a scan provided that they are filtered out before being digitized by the computer. For the microscope used in these studies, this was accomplished with a low-pass filter usually set to a 300 Hz - 1 kHz cutoff. The signal was digitized by a 16 bit Data Translation 2823 A/D board. Typical data acquisition rates were on the order of 200 Hz.

High voltage amplifiers

The Data Translation also has D/A outputs which were addressed with “home-written” software in order to output x- and y- voltages corresponding to the desired scan size. The intrinsic piezo gain for the x- scanner (cross) was 12.5 Å/V while that for the y-scanner (tube) was 14.5 Å/V. This being the case, high-voltage, low-noise amplifiers were used to increase the output voltage of the D/A board. With the high voltage amplifiers as much as ± 220 Volts could be applied to the scanner corresponding to a maximum scan size for this microscope of about 1.2 μm on a side (with equal and opposite voltages being sent simultaneously to the +x (+y) and -x (-y) scanner electrodes respectively). To help maintain lower noise levels, the output of these high voltage amplifiers was also passed through low pass filters with RC’s on the order of 10^-3 s to
10^4 s. The z-output voltage of the FCU was also passed through a filtered high voltage amplifier so a large dynamic z-range could also be obtained.

**Tilt compensator**

This large dynamic z-range is often necessary because samples are generally not positioned exactly normal to the tip. During the scan then, the FCU ends up putting a progressively higher offset voltage on the z output to have the tip to track the plane of the surface. This tilted sample plane is usually sloped in both the x- and y-directions. The offset can create a problem for the A/D card in that the card's acceptable input voltage range may be exceeded. To compensate for a tilted sample, additional electronics were designed so that a portion of the x and y scan voltages (selected manually) could be continuously added to the z-output voltage of the FCU. In this way, a sample tilt could be automatically subtracted as the scan was being taken. This alleviates the burden on the FCU to supply the required offset, and hence keeps the z-voltage out in an acceptable range for the computer to measure.

*Tip alteration electronics*

The electronic behavior of tips can vary greatly over time and scanning conditions. Spontaneous rearrangements can occur which may increase or decrease image resolution. Often the tip is purposely modified in the hope of improving its resolution. For serious tip problems, hard crashes are often necessary to dramatically change tip morphology. These methods include walking the tip into the sample, scraping the tip
against the Mo sample clips, and locally melting the tip by passing a high density field emission current through it. Often, however, only a slight atomic rearrangement is necessary at the end of the tip to increase image resolution. This alteration can generally be accomplished with a short voltage pulse to the sample (a few volts for a few milliseconds) or a sample bias ramp (up to ~ 10 V over a few seconds). For convenience, an electronic box with trigger switches for each of these operations was integrated into the rack of control electronics.

2.3 UHV system specifications

An overview of the entire vacuum system is shown in Fig. 2.9. The microscope and 6” flange assembly are positioned at the top of a six-way, ultra-high vacuum chamber. The chamber is initially pumped down to the 10^{-5} torr range with a Balzers turbo molecular pump. After closing off the roughing valve, the system is opened to a 200 liter \cdot s^{-1} Perkin-Elmer ion pump isolated from the chamber with a VAT gate valve. Base pressures in the chamber (after 24 hr of baking the system at 150°C) are less than 2\times 10^{-10} torr as determined by a nude ion gauge. Also mounted in the chamber is a Spectramass Dataquad residual gas analyzer (RGA) which is based on quadrupole mass spectrometry. Of the gas components that make up the base pressure, the largest is H_{2}, then H_{2}O, CO, and CO_{2} as discussed in section 2.6. On the facing and left side of the six-way cross are glass viewports which are used when positioning the samples and when measuring the temperature of samples with an infrared pyrometer.
In addition, the system is equipped with a precision leak valve (Varian) with which oxygen can be introduced into the chamber. The oxygen is delivered to the leak valve through a high vacuum, all metal oxygen sub-system that is directly attached to the O₂ cylinder. This sub-system is pumped-out, baked, and replenished with a new dose of oxygen every few months. This dose is supplied by opening the cylinder’s valve for an instant. This introduces > 1 atm of O₂ into the sub-system, and since very little O₂ is used during an oxidation, a pressure > 1 atm can be maintained in the sub-system at all times.

2.4 Tip preparation

Most of the tips used in these studies were prepared in our laboratory using electrochemical etching. For this procedure, 10 mil tungsten wire was positioned in a 1 molar NaOH solution with a metal electrode. As current is passed between the electrode and the wire, ions attack the wire at the meniscus, and the tip is formed when the wire is etched through (Fig. 2.10). Sometimes these tips were annealed by current heating to a dull orange glow before being placed in vacuum. It was found, however, that reasonable tips stability and similar results could also be achieved by omitting this annealing step. Occasionally commercial Pt-Ir tips would be used, but no advantage was observed in imaging.
2.5 Sample preparation

The silicon wafers used in these studies were purchased from Virginia Semiconductor. Among samples examined were n-type (phosphorous) and p-type (boron) doped wafers including wafers with varying degrees of resistivity as well as surface miscut. Sample resistivities were generally high to facilitate easy resistive-current heating of the wafers in situ as well as to insure an emissivity that was relatively independent of temperature over the range 20 - 1300°C. This constant emissivity (0.7) is necessary for accurate temperature measurements using an infrared pyrometer. Resistivities generally ranged from 0.005 Ω cm to 0.5 Ω cm. Sample miscuts for most studies were ~0.2° away from the perfect crystalline plane, but wafers nominally specified at 0.0° and 3.0° were also studied to examine step density effects on oxidation. The very low miscut samples were actually found to have ~0.1° miscut not 0.0° as specified. In addition, miscut directions for Si(001) samples were generally in the [110] direction to obtain well defined S_A and S_B steps as stated in section 1.2.

Samples were prepared by first cleaving the commercial silicon wafer to the necessary dimensions (~ 20 x 6 x 0.4 mm) for incorporation into the clips of the sample stage. This was accomplished using a diamond-tipped scribe to make the original mark and then cleaving the wafer along this mark by pressing on one side with plastic tweezers. It is important to note that metal-tool contact with the silicon was always avoided to avoid metallic contamination. The samples were then rinsed with methanol, air-dried
with nitrogen and inserted into the clips of the sample stage. Since samples were thermally "flashed" to high temperatures in situ, no additional pre-cleaning was necessary.

Once in ultra-high vacuum (after system bakeout), both samples on the stage were outgassed at ~780°C for at least a 12 hr period. This removed many gas-phase contaminants which adhered to sample and to the sample stage during the bakeout. It should be noted that this temperature is low enough to preserve the passivating, native oxide layer which is on the wafer as received from the company. This outgassing helps to minimize the rise in pressure accompanying the initial flash of the sample which in turn minimizes the initial defects on the surfaces being scanned.

After allowing the samples and stage to cool for a few hours, a single sample is flashed with all hot filaments in the system turned off. In this process the native oxide layer is removed, and the surface reconstructions noted in the introduction are formed. The flash sequence most commonly used is as follows:

1. Slow rise to ~840°C then cool quickly to room temperature (RT).
2. Rise quickly to ~1280°C, hold for ~5-10 seconds, cool quickly to RT
3. Repeat step (2) 4-6 times until the maximum pressure (as measured by the ion pump current) is in the low 10⁻⁹ torr range.
4. Rise quickly to 1240°C, cool immediately to ~940°C, hold for 30 s, then cool slowly to RT. Pressure during this step should stay in the 10⁻¹⁰ torr range.
Between each high temperature step the sample is allowed to cool for 2 min so that the system may return to the base pressure.

This process would reproducibly result in clean silicon surfaces (on both (001) and (111)) with very little if any evidence of contamination. Starting defect densities were generally less than 2% of the surface. Often the defect density would go down upon subsequent flashes. This was attributed to the fact that the system was getting progressively cleaner with each flash. Samples could be re-flashed almost daily for periods up to ~ 2 months before showing signs of increasing defect density. This helped remove sample-to-sample variability, and allowed for oxidation experiments to directly test $T_s$, $P_{ox}$, and $D_{ox}$ dependencies on the same piece of silicon. Even with sample changes, however, different batches of Si wafers showed similar behavior.

2.6 Exposure procedures

After the clean surface was characterized with STM, oxidations were performed by raising the sample back to the heating stage, heating to the desired temperature ($T_s$), and backfilling the chamber to the desired partial pressure (see section 2.6) with research grade $O_2$ (99.999 % pure) from Matheson Gas Products. All hot filaments were off during the exposure to minimize the effects of $O_2$ ionization which leads to enhanced
oxidation from atomic oxygen. The total oxidation times were measured to within a few seconds.

The temperature was usually quenched to RT within 5 seconds after the leak valve was closed at the end of a dose. Occasionally, as a check, the temperature would be allowed to stay elevated for as much as 30 min after the oxidation to see the effect this would have on resulting surface morphology. It was found that hold times as high as 30 min had very little effect on large scale surface morphology. All STM scans were taken at room temperature, and samples were re-flashed after each exposure (except in the case of RT studies which examined the evolution of a particular area after subsequent doses).

For extended dose experiments a slightly different oxidation procedure was used. In this procedure, the sample was oxidized directly from the flash and was briefly "pre-etched." Essentially this exposure was like the flash procedure described in section 2.4. In step (4), however, after sitting at 940°C for 30 s, O₂ was then introduced into the chamber at 6x10⁻⁸ torr for 14 min while the temperature remained at 940°C. This step produces only surface etching and removes the top 2-3 layers of silicon. After this pre-etch, the sample is cooled further to the oxidation temperature (640-690°C) and exposed to O₂ (at 3x10⁻⁸ - 1.2x10⁻⁷ torr). Following the desired dose, the sample is again quenched to room temperature and scanned. Occasionally, samples would be quenched directly following the 940°C etch and scanned, verifying that this step does not itself nucleate oxide clusters. This is consistent with the fact that these oxidation conditions are within the "etching only" regime as predicted by the commonly accepted critical condition diagram in Fig. 1.9 In addition to a somewhat greater reproducibility, this "pre-etch"
procedure generally resulted in slightly fewer (within a factor of 2) nucleated oxide clusters than with the first procedure in which the clean surface is scanned before oxygen exposure. We postulate that the reason for this is that during the time it takes to scan the clean surface, additional defects can form on the surface (either from the tip or gas-phase adsorbates) which may enhance subsequent oxide nucleation.

2.7 Temperature and Pressure measurements

The $O_2$ pressure during each dose was determined by monitoring the ion-pump current which had been previously calibrated against a standard ion gauge over a range of oxidation pressures of interest. We estimate a ±20% uncertainty in the pressure measurements relative to each other, and a larger (±50%) uncertainty in the absolute measurements. Since both these techniques measure the total gas pressure in the system and we are really only interested in the oxygen partial pressure, we also used the RGA to determine the specific oxygen partial pressure during an test exposure. Although the absolute partial pressures were never normalized to correspond with the true overall system pressures, the relative quantities of different gases in the system may be considered accurate. This analysis (Fig. 2.11) showed that the $O_2$ peak was about 10 times higher than the next largest peaks which were $H_2$ and $O$. It should be noted that the presence of atomic oxygen is only related to the cracking of molecular oxygen by the RGA's filament and would not be present during a regular oxidation when all hot filaments are off. The hydrogen peak, although almost 10% of the oxygen peak, is not too much of a concern
since experiments show that molecular hydrogen has a very low sticking coefficient on silicon at our oxidation temperatures in the range of 600 - 700°C.\textsuperscript{104} The next largest peak is CO which is only \textasciitilde 8\% of the oxygen peak. Since carbon contaminants are known to affect surface morphology on silicon during high temperature processing steps, this is really the only peak we need be concerned about. The other carbon related peak, CO\textsubscript{2}, is about 5 times smaller than the CO peak. Water is known to enhance oxidation, but as can be seen from Fig. 2.10, it is only about 1.5\% of the oxygen peak so these effects should be minimal. In addition, it is possible that some of the gas registered by the RGA may originate (via stray sputtering) from the gas analyzer itself (especially H\textsubscript{2}O and CO). Given these facts, the spectra in Fig. 2.11 would be the worst case scenario during an actual oxidation. Nevertheless, this breakdown of gas components will be referenced when discussing possible contamination-related oxidation effects.

For all experiments, silicon substrate temperatures were measured with an infrared pyrometer from E\textsuperscript{2}Technology Corp. (Model 7100GP, sensitivity range 260 - 1650°C). The pyrometer was placed just outside the front glass viewport and measured the sample's infrared radiation to determine its temperature. The pyrometer operates between 2.0 and 2.5 \textmu m which is right at the edge of the glass window's transmittance curve (Fig. 2.12(a)),\textsuperscript{105} so infrared radiation from the sample is somewhat attenuated. To account for this effect, samples were measured in air with and without various viewports present so differences in temperature due to viewport attenuation could be noted. The summary of these results (Fig. 2.12(b)) shows that in all cases the measured temperature is
lower than the temperature without the viewport and the difference increases as temperature is increased. Although many viewports are noted in Fig. 2.12(b), only the 6” flange was relevant to the oxidation experiments presented here.

In an effort to calibrate the pyrometer reading with absolute temperatures, eutectic samples were observed for their characteristic transition with the pyrometer. This experiment, done by D. Jones, indicated a 42°C underestimate for the Ag-Si eutectic transition at 855°C and a 89°C underestimate for the Al-Si transition at 577°C. In addition, pyrometer calibration was done ex situ in a high temperature furnace where type K thermocouples could be easily attached to a sample holder and cross referenced with the furnace temperature and then compared with the pyrometer reading. The data from these experiments are shown in Fig. 2.13. From these data we conclude that the temperature measurements reported here have very good relative accuracy (within 1-2 degrees) and probably underestimated the true sample temperature on average by about 40°C. This difference should be noted, since all temperatures reported in previous manuscripts (Refs. 90-94) referred to the temperature as read by the pyrometer through the 6” viewport. In this manuscript we will report the corrected absolute temperatures including viewport effects in an attempt to be as accurate as possible.

For some experiments, a temperature gradient was established across the sample during oxidation and the temperature-vs-position profile was measured with the pyrometer noted above. For this procedure the pyrometer was mounted on a translation stage to maintain a high level of accuracy. For all measurements the pyrometer integrates the radiation intensity over a spot size of 1.7 mm x 1.7 mm on the sample (when the
pyrometer is positioned at its normal focal length of about 7” away from the sample). The edge to edge temperature distribution was measured with about 10 points using the translation stage and was later matched with the micrometer position of the sample translator. By touching the tip at one edge of a sample clip and noting the sample micrometer position, a reference point was established which could be used to determine the specific temperature location that the tip was over during a scan. A typical temperature profile is shown in Fig. 2.14. Different areas of the same sample (after a single oxidation) could then be scanned to directly monitor the temperature dependence of the oxide nucleation.
Figure 2.1 Energy level schematic of the tunneling process. The tunnel current is exponentially dependent on the separation of the tip and sample and dependent on the availability of degenerate filled and empty electronic states at bias voltages around the Fermi energy, $E_F$. Here the tip is assumed to be an ideal metallic tip with work function, $\phi_T$, and the sample to be a material with work function, $\phi_S$, and a non-uniform local density of states (LDOS) [from Ref. 100].
Figure 2.2 Schematic overview of STM. Voltages are applied to the x- and y-piezos in order to raster scan the tip across the sample's surface. The feedback control unit measures the tunnel current, $J_T$, and adjusts the height of the tip over the sample in order to keep the tunnel current constant. Both topographical and electronic features on the surface can affect $J_T$ [after Ref. 52].
Figure 2.3 Schematic of early STM designed by Binnig and Rohrer [from Ref. 101]. (a) basic mechanical design. (b) 10000x magnification of the tip-sample junction. (c) additional 10000x magnification of the same junction suggesting atomic configurations and electronic state density contours.
Figure 2.4 The Besocke walker. (a) Schematic overview of the tube arrangement to accommodate a triangular sample stage. (b) Schematic of how equal and opposite applied voltages to opposing electrodes cause the tubes to bend [from Ref. 96]. In operation, the piezo tubes are made to bend slowly in one direction causing the sample stage to move with them, then retract quickly back to the vertical position causing the sample stage to inertially slip and remain in its previous position. With the use of a quadrant tube, the sample may be translated in any of the four directions.
Figure 2.5 STM scanner components. (a) cross-piezo scanner to achieve x- and z- motions. (b) example of a quadrant, outer electrode piezo tube that achieves all three coordinate motions which can be used without the cross scanner. A similar single outer electrode tube is mounted in the center of the cross scanner to create the y-motion. This cross plus tube configuration is the scanner design used in this study. (c) proprietary tip carousel with tips represented schematically by black lines. This rotatable cap sits on top of a magnet which is attached to the top of the single y-tube scanner. This provides the opportunity to use six different tips without bringing the system up to atmosphere.
Figure 2.6 The sample stage. This stage is supported by three support hooks which hang from three opposing support hooks connected to an ex situ x-, y-, z-manipulator as shown in Fig. 2.7. When the sample is lowered onto the Besocke walker, the hooks decouple allowing the sample to “walk” freely.
Figure 2.7 Picture of the UHV-STM used in these experiments. Photo was taken through the system's viewport. Here the sample stage is hanging above the piezo walker.
Figure 2.8 Comparison of feedback response modes to a step function input. (a) proportional response with cutoff, (b) integral response only, (c) comparison of integral plus differential to integral only and proportional with cutoff. For our studies a steady-state offset in the error signal was not important, so the proportional mode with cutoff was used as marked by the arrow in (a). See text for a detailed discussion. These graphs were calculated by Park and Bartlett and published in Ref. 97.
Figure 2.9 System overview
Figure 2.10 Tip Preparation. (a) Schematic of the etching process [from Ref. 96]. (b) SEM photograph of a resulting tungsten tip. Tip base is 0.01" diameter.
Figure 2.11 RGA spectra. (a) typical system background dominated by hydrogen, CO, water, and CO$_2$. (b) and (c) RGA profile during oxidation. O$_2$ is the dominant peak during oxidation by more than an order of magnitude. During oxidation, the RGA filament is off, so mass 16 (atomic oxygen) should be substantially reduced.
Figure 2.12 Viewport effects on temperature measurement. (a) transmittance curve for the typical glass viewport used in these experiments [from Ref. 105]. (b) temperature measurement variations for various viewports used in the laboratory.
Figure 2.13 Temperature calibration. Eutectic and oxidation furnace results. On average we estimate that the pyrometer reading is about a 40° underestimate of the true temperature.
Figure 2.14 Typical sample temperature profile on gradient sample. The solid line is a second order fit to guide the eye. Gradients like this one were created by having one bad sample clip create a “hot spot” on the sample.
CHAPTER 3

RESULTS: ROOM TEMPERATURE EXPOSURE AND ANNEALING

3.1 Room Temperature Oxidation (The Passive Oxidation Regime)

3.1.1 Si(111)-(7x7): Observations

As a starting point and to confirm consistency with previous room temperature oxidation measurements, STM experiments on Si(111)-(7x7) were performed. Consistent with previous studies, the primary conclusions are that at least two types of reacted species initially form. Figure 3.1 shows a sequence of successive room temperature oxidation doses (on the same area) which clearly shows both bright and dark reacted species. Consistent with the work of Pelz and Koch, a preference of 1.5:1 for bright sites reacting at corner adatom locations was observed, while a preference of 1.2:1 for dark sites reacting at corner adatom locations was observed. Also observed unambiguously is the conversion of bright sites to dark sites (marked by arrows in Fig. 3.1) which tends to skew the counting of the dark site positional preferences. If we examine the location of dark sites that formed without a bright site precursor there is a 1.2:1 preference for reaction with center adatom
locations. This result suggest two distinctly different reaction pathways for dark site formation, and again is the same result obtained by Pelz and Koch. Furthermore, we find that bright corner sites and bright center sites convert to their respective dark site with equal probability.

The dark species is more stable than the bright, and dominates at higher temperatures and O₂ exposures.⁴⁶,⁴⁷,⁷⁶ We define a "sticking" coefficient $s_0^d$ ($s_0^b$) as the fractional probability that an in-coming O₂ molecule will react to form a dark (bright) site. From the low dose data in Fig 3.1, we find that $s_0^d = 0.0073$ and $s_0^b = 0.065$. At higher doses it has been found that bright site formation is suppressed and oxidation proceeds through the formation of dark sites. Measurements taken at higher O₂ exposures indicate that the dark species tend to "cluster" on the surface, indicating enhanced reactivity adjacent to reacted sites.⁴⁴,⁴⁷ Under these conditions we measure a single sticking coefficient $s_0 = 1.4 \times 10^{-2}$ (±25%) at room temperature.

3.1.2 Si(001)-(2x1): Observations

Again to check for consistency in our experiments and with other groups, room temperature Si(001)-(2x1) oxidation was examined. In general, reported studies of room temperature oxidation behavior were also verified in this study. The primary observation is that oxygen sticks primarily on the Si(001) surface at defect sites, particularly the c-type defect site. Figure 3.2 shows that after ~2.4 L of oxygen all original c-type defects on the starting surface have reacted with the oxygen. According to analysis of our data,
we find at least an 8:1 preference for oxidation at an existing defect site as opposed to clean 2x1 reconstructed sites. In addition, we also find that some reacted areas of the surface have an extremely small density of states at typical scanning voltages. This results in very deep "holes" (primarily electronic as opposed to topographical) into which the tip must be lowered to maintain a constant tunnel current. This often induces a change in the tip's structure, since the tip may be imbedding in an insulating oxide which has a much reduced density of states near the Fermi level. An example of a moderately deep (>1 ML) can be seen in the line scan of Fig 3.2. We have also found that the depth of these "holes" is influenced by the tip's structure indicating that these anomalously deep holes may only be visible with certain tips and not others. Occasionally holes as deep as 5 ML have been observed.

Like Cahill and Avouris, we too observed evidence of Si ejection onto the surface. The line scan of Fig 3.2 shows a raised bump which is 1.4 Å high and thus is likely an ejected silicon atom or dimer. Studies show that many of these raised protrusions do in fact line up to form epitaxial islands upon annealing. It will be shown in Chapter 4 that exposure to oxygen at higher temperatures often results in a single dark defect with two raised protrusions surrounding it which may be similar to this Si ejection seen at room temperature.

Another feature observed which to date has been unreported is a four-fold symmetric defect. This defect is seen only after exposure to oxygen and seems to initially occur only on previously clean 2x1 reconstructed areas of the surface. The defects (circled in Fig 3.2 and shown close-up in Fig. 3.3) are made up of 4 slight depressions
located on a dimer row. To determine the position of this defect relative to individual
dimers, it is necessary to appeal to the concept of buckling on Si(001)-(2x1) surfaces as
introduced in section 1.2.

By correlating the depressions with the buckling periodicity which proceeds
through this defect, the four depressions are observed to be located over the atomic
positions of the dimer as can be deduced from Fig. 3.3. Interestingly, the buckling
apparently has no effect on the stability of the reacted site in that the depressions are still
apparent even with the buckling. Only a few positions can be consistent with the four­
fold symmetry of the structure.

If it is assumed that only one O$_2$ molecule is responsible for this reacted site, then
the O$_2$ molecule must be symmetrically located over the dimer row, either perpendicular
or parallel to the dimer direction (as suggested by the dotted lines in Fig. 3.3). If the
molecule has dissociated, it is possible that the resulting atoms have inserted into adjacent
dimer bonds or are bridging adjacent dimer atoms as shown by the solid lines in Fig. 3.3.
Interested theorists may use this information with the appropriate calculations to try to
identify this particular species.

3.2 Annealing: Line Defects

In the course of performing annealing studies after room temperature oxidations and
higher temperature exposure to oxygen, we found the occurrence of very distinct line
defects under certain experimental conditions.$^{106}$ This section will give a brief overview of
these defects and the resulting 2xn reconstruction that occurs when these lines arrange themselves on the surface. Although not crucial for an understanding of silicon oxidation, the lines were occasionally observed after a high temperature oxidation or anneal and are thus discussed here for completeness. It should also be emphasized that the occurrence of these line defects was not prevalent during the course of the quantitative oxide cluster analysis that will be presented in Chapters 4 and 5.

For a number of years there have been reports\textsuperscript{107,108,109,110,111,112,113,114} of a "2xn" structure on the Si(001) surface, with n typically in the range of six to ten. This structure was attributed to a variety of origins, including oxidation,\textsuperscript{109} thermal quenching,\textsuperscript{107,109,112} sputter etching,\textsuperscript{109} and surface strain.\textsuperscript{110} However, this structure often could not be reproduced in different laboratories, suggesting that some form of contamination may be involved. In fact metal contamination (in particular Ni) was identified as one source of this 2xn structure.\textsuperscript{108,111,113} Niehus et al.\textsuperscript{113} showed that the 2xn structure due to Ni contamination appeared in real-space STM images similar to rows of missing dimers (RMD's) oriented perpendicular to the direction of dimer rows on the Si(001) 2x1 surface. Another STM study by Sakurai et al.\textsuperscript{114} reported that repeated anneals to 1200°C could also produce a highly-defected, quasi-ordered 2xn structure even when no Ni could be detected by Auger spectroscopy. The 2xn structures found in these past studies in general tended to be irreversible in the sense that they became more prominent with successive thermal annealing cycles. More recently, Zandvliet and co-workers\textsuperscript{115,116} have reported that "line defects" similar in appearance to RMD's can result when Si(001) surfaces are ion-sputtered at room temperature and then annealed at temperatures in the range 600 - 800°C. Nickel
contamination was ruled out as a possible cause because the line defects could be reversibly removed by annealing to temperatures greater than 950°C. Feil et al.\textsuperscript{116} postulated that these line defects were formed by thermally activated migration and ordering of sputter-induced vacancies.

In the course of our own STM measurements of the oxidation-induced etching of the Si(001) surface, we have also observed surface structures consisting of line defects (similar in appearance to RMD's) forming a quasi-ordered \(2\times n\) structure. Upon further study, we determined that these structures were \textit{primarily due to a build-up of adsorbed gas contamination on the sample surface at room temperature, followed by an anneal in the temperature range 540 \textdegree{C} - 840 \textdegree{C}.} The density of these line defects scaled (roughly) in proportion to the density of adsorbed contaminants, which in turn was proportional to the time the sample sat at room temperature. These line defects could be eliminated by annealing the sample at temperatures above 940\textdegree{C}, indicating that Ni contamination was not the origin. These measurements show that a strictly gas-phase adsorption process can lead to the creation of \(2\times n\) - type surface structures on Si(001) upon annealing, without the need for Ni, thermal quenching, or ion sputtering. In time, this contamination effect became much less noticeable, probably through an elimination of the contamination source during repeated baking of our vacuum system. Although we have not identified the particular contaminant(s) responsible for these line defects, we have found that adsorbed \(\text{O}_2\) and \(\text{H}_2\text{O}\) do not produce as dramatic alignment behavior as seen with the unknown contaminant.
Our system’s residual gas analyzer (RGA) had been at the factory for repairs and was re-installed on the vacuum system shortly before the contamination effects were first noticed. In addition to the usual peaks for H₂, H₂O, CO, and CO₂, we also observed a large (~10⁻¹¹ torr) peak at mass 19 (F) (Fig. 2.11). At the time, we believed that this was due to local outgassing at the RGA, a commonly observed effect with many residual gas analyzers. However, we cannot rule out the possibility that significant amounts of F were in the vacuum system, possibly even coming from the RGA itself. In time, this mass 19 peak became much less prominent.

Figure 3.4 shows an example of the line defects which were observed during our early oxidation experiments. Fig. 3.4 (a) shows a region of a Si(001) surface after sitting for 19 hours in the UHV system at room temperature. The high defect density seen on the surface is mostly due to a build-up of adsorbed contaminants. Fig. 3.4 (b) shows a different region of the sample after it was heated at 640°C for 13 minutes in the presence of 9x10⁻⁹ torr of O₂. This figure shows clear line defects (appearing as RMD's), which form a quasi-periodic array with average spacing of roughly 12 to 14 surface lattice units (a₀=3.84 Å). Some of these line defects extend up to 170 Å in length and typically have a width of 1 or 2 a₀. The line defects appeared as "depressions" in the STM images at both positive and negative bias, with a typical depth of about 0.9 Å (~2/3 of a single step height).

Although we initially suspected that oxidation-induced surface vacancies were responsible for these line defects, subsequent experiments indicated that the true cause was the high initial defect density and the 640°C heat treatment. This can be seen in Fig. 3.5, which shows a series of images of a different sample in which only simple annealing was
involved. Fig. 3.5(a) shows a region of the sample after sitting for 24 hrs at room temperature following a flash. Most of the defects seen in this image are again due to adsorption of background contaminant gases after the flash. Fig. 3.5(b) shows a different region of the same sample soon after a 3 min anneal at 840°C. A quasi-periodic array of line defects is clearly evident. These line defects can be reversibly eliminated by annealing at temperatures above 940°C, again indicating that Ni contamination is not the cause. This is seen in Fig. 3.5(c), which shows that a flash at 1290°C returns the surface to a state with very few line defects and a low over-all defect density (~1.2% dimers defected). This entire contamination-annealing process can be repeated. Fig. 3.5(d) again shows line defects after an 840°C anneal done 11 hours later. Fig. 3.5(e) shows the surface after another 12 hours (with no annealing done in between), clearly indicating the build-up of surface contaminants. Fig. 3.5(f) shows that a 5 min anneal at 840°C again leads to distinct line defects. Finally a subsequent flash at 1290°C again returns the surface (not shown) to a low-defect state similar to that seen in Fig. 3.5(c).

We have found that a build-up of adsorbates and annealing are both required to produce these line defects. If a surface with low initial defect density (such as Fig 3.5(c)) was annealed at 540 - 840°C immediately following a flash, no line defects were found, and the overall point-defect density was unchanged. If, however, a substantial number of adsorbate-related defects were allowed to accumulate, then annealing led to formation of line defects as well as a general reduction in the overall defect density. This is illustrated in Fig. 3.6, which shows that the density of defects found in lines after an anneal (in the range 540 - 840°C) was roughly proportional to the elapsed time from a 1290°C flash. A similar
trend was found for other sequences of anneals and hold times, provided all anneals were in the range 540 - 840°C. The density of defects in lines was greatly reduced by a 940°C anneal, and a 1290°C flash eliminated the lines altogether. If one assumes an adsorbate sticking coefficient of unity and that two adsorbate molecules are required to create each defected dimer that ends up in a line, then the build-up rate shown in Fig. 3.6 implies an adsorbate partial pressure of about $3 \times 10^{-13}$ torr.

Over the course of these measurements, we did observe a very strong variation in the rate at which contaminants accumulated on the surface. During the time that Figs. 3.4 and 3.5 were measured, a marked increase in surface contamination could be observed after a time as short as 10 hours. At a later time, many days were required to build up a similar contaminant density. Furthermore, the contaminants that did accumulate in this later case showed a greatly reduced tendency to form line defects when the sample was annealed. This strongly suggests that the line defects were due to a particular gas-phase contaminant which was present in the system during the earlier measurements.

After these contamination effects became less severe, we performed several tests which showed that adsorption of $O_2$ or $H_2O$ does not lead to nearly as enhanced line defect structures. Figure 3.7 shows the results of one such test. Figure 3.7(a) was measured immediately after a clean Si(001) surface (such as that shown in Fig. 3.5(c)) was exposed at room temperature to $O_2$ for 180 s at a pressure of $2.3 \times 10^{-8}$ torr. The dark oxidized sites and "ejected" Si seen in Fig. 3.7(a) are consistent with the room-temperature oxidation behavior reported by Cahill and Avouris. The oxygen dose was chosen to create a defect density similar to that seen in Fig. 3.4(a) and Fig. 3.5(a). Figure 3.7(b) is characteristic of the
surface after a subsequent 3 min anneal at 640°C. The overall surface defect density is reduced, but few line defects of significant length are formed. Similar experiments also showed that O\textsubscript{2} exposure at 640°C produced very few line defects, provided the starting surface was contaminant-free. Experiments with adsorption of 0.07 L of H\textsubscript{2}O followed by a 10 min 640°C anneal (Fig. 3.8) produces a surface with a high random defect density, but with very few in straight lines and an overall behavior very different from that seen in Fig. 3.4 and Fig. 3.5.

Martin \textit{et al.}\textsuperscript{109} reported that a 2xn structure could be produced on Si(001) by a rapid thermal quench (≈250 K/s) from elevated temperatures. We tried rapid quenching directly from 1290°C, but found that a clean surface with very low defect density (≈1% defected dimers) was produced, provided the heating and cooling was done quickly enough to keep the background pressure in the 10\textsuperscript{-10} torr range. However, if we kept the sample at 1240°C for 2 min followed by 15 min more at 1040°C and then quenched to room temperature (the actual procedure used by Martin \textit{et al.}), the background pressure rose into the 10\textsuperscript{-4} torr range and a high density of random surface defects resulted. This defected surface was then annealed at 640°C for 10 min, and distinct line defects were again seen. During a subsequent extended heating test, we found the main gas components during this pressure burst to be (in descending order) CO\textsubscript{2}, CO, H\textsubscript{2}, and H\textsubscript{2}O, but no noticeable increase in the mass 19 peak.

There appears to be a strong similarity between the line defects reported here and the sputter-induced line defects reported by Zandvliet and co-workers,\textsuperscript{115,116} in particular regarding their behavior during thermal annealing. They could in principle be the same
provided the adsorbates in our study lead to the creation of surface vacancies at temperatures less than \( \approx 540^\circ C \). In this case the vacancies could migrate and align according to the mechanism proposed by Feil et al.\textsuperscript{116} Our tests with \( O_2 \) and \( H_2O \) adsorption suggest that vacancies created by desorption of \( SiO \) at elevated temperatures are not directly responsible for the line defects. Fluorine remains a possible candidate, particularly since it is known that sub-monolayer doses of \( F \) on \( Si(001) \) can spontaneously etch the surface for \( T > \approx 500^\circ C \) (primarily through the desorption of \( SiF_3 \)).\textsuperscript{117} However, \( F \) is so reactive that one would think that any excess \( F \) in the system would quickly react with the chamber walls and not remain in the gas phase (note that no hot filaments were operated during extended experiments).

We should note that our experiments alone do not rule out the possibility that the line defects are actually aligned \textit{adsorbates} (rather than aligned \textit{vacancies}) which simply appear dark in STM images due to a reduced density of states near the Fermi level. Since hydrogen desorbs rapidly from \( Si(001) \) at temperatures above \( 500^\circ C \),\textsuperscript{104} we would expect very little hydrogen left on the surface after an \( 840^\circ C \) anneal, thus making it an unlikely candidate. \( CO \) and \( CO_2 \) should be considered since they were present in the vacuum system at all times that distinct line defects were observed.

To summarize this section, we have observed that a build-up of gas-phase adsorbates on \( Si(001) \) followed by mild annealing at temperatures in the range \( 540 - 840^\circ C \) can lead to a quasi-periodic array of line defects. These line defects can be eliminated by annealing at temperatures above \( 940^\circ C \). Molecular \( O_2 \) and \( H_2O \) do not produce nearly as dramatic alignment behavior indicating that another gas phase contaminant is most likely
the cause. Whatever the contaminant is, it seems likely that it results in vacancies which are the species which actually align. Since O₂ and H₂O can cause vacancies, these species may still be able to cause line defects under conditions (dose, temperature) untested by this study.

Finally we again emphasize that the contaminant was not prevalent during the course of subsequent experiments and the quantitative analysis presented in the next chapters. In fact, the appearance of the lines decreased with time (in about 2-3 months), as subsequent bake-outs and pump-downs made the system progressively cleaner. Apparently, the source of the contaminant was removed by this process, and such distinct lines have not been observed in the system since that time.
Figure 3.1 Room temperature Si(111)-(7x7) oxidation sequence. The circled bright-site defects serve as position references. All images are 290 Å x 290 Å. Both bright and dark reacted sites are visible. Total doses are 0.0 L, 0.2 L, 0.4 L, and 0.7 L for (a), (b), (c), and (d) respectively. Arrows indicate bright site conversion to dark site.
Figure 3.2 Room temperature Si(001)-(2x1) oxidation sequence. Preferential c-type defect reactivity is evident. Novel 4-point symmetric defects and their evolution are circled. The line scan is indicated by the dotted line in the STM image at 2.4 L.
Figure 3.3 Close-up of the four-fold symmetric defect. (a) reference image. Spacing between dimer rows is 7.68 Å. Spacing between dimers is 3.84 Å. (b) The solid line marks the buckling periodicity. The arrows point to the atomic positions in adjacent dimers, and the dotted circles highlight the four depressions of the defect. (c) and (d) show possible positions for dissociated oxygen atoms and their possible bonding orientations.
Figure 3.4 Line defects after oxidation. (a) 370 x 370 Å² area ~ 19 hrs after sample flashed at 1290°C. (b) Same sample after heating at 640°C for 13 min in 9x10⁻² torr of O₂, scan area 670 x 470Å².
Figure 3.5 Line defect cycling. Sequential images of a sample showing effects of adsorbate build-up and heat treatment. (a) 24 hrs after a flash with one intermediate 640°C anneal, (b) after subsequent 3 min anneal at 840°C, (c) after re-flash, (d) after 5 min 840°C anneal 11 hrs later, (e) 12 hrs later with no intervening heat treatment, (f) after 5 min 840°C anneal. Scan areas about 600x770 Å².
Figure 3.6 Density of defected dimers found in lines after an anneal vs elapsed time since a 1290°C flash. Each anneal was 5 min at indicated temperature. For counting purposes, a "line" is defined as three or more adjacent defected dimers, and all line defects are assumed to have a single dimer width. At least three separate areas were measured for each point to determine the average value and error bars.
Figure 3.7  Room temperature exposure to oxygen then anneal. (a) surface after exposure to O$_2$ at 2.3x10$^{-5}$ torr for 3 min. The starting surface was similar to Fig. 3.5(c). (b) Same sample after annealing at 640°C for 3 min. Image sizes are ~ 600 Å x 770 Å.
Figure 3.8 Room temperature exposure to H$_2$O followed by anneal. (a) Clean Si(001)-(2x1) surface, 600 Å x 770 Å (b) different area (590 Å x 476 Å) of same sample after a 0.07 L dose of water vapor. (c) after subsequent anneal at 640°C for 10 min, 600 Å x 770 Å. (d) same conditions and size as (c), but different area of sample. Clearly a large amount of etching has occurred evident by the large etch pit and two step “fingers” which each cover an antiphase boundary (marked by arrows).
CHAPTER 4

RESULTS: ELEVATED TEMPERATURE

4.1 Si(111)-(7x7)

4.1.1 STM Observations

In Chapter 3, both dark and bright reacted sites were shown to occur on the Si(111)-(7x7) surface after exposure to oxygen at room temperature. It was shown by others that the dark sites were not missing adatoms, but were reacted species with a locally reduced density of states at the Fermi energy. Upon exposing the surface to oxygen at higher temperatures, similar behavior was found.

Figure 4.1 shows a Si(111) surface exposed to 3.4 L of O\textsubscript{2} at 440°C. Oxidation at 440°C creates reacted adatom sites similar in appearance to the dark species discussed above, with a value $s_{q} = 2 \times 10^{-3}$. There appears to be an increase in the degree of clustering of reacted sites as compared with room temperature, but there are still many individual reacted sites scattered over the surface as well. We did not find evidence of bright sites with the tips and bias voltages used under these elevated temperature conditions. This is
consistent with the work of Pelz and Koch which showed that annealing a sample (in the 
range of 350 - 400°C) that had been exposed to oxygen at room temperature reduced the 
number of bright reacted sites. Their conclusion was that the bright reacted site was the 
precursor in a two step oxidation process which was facilitated at higher temperatures and 
hence lead to reduction in the number of observed bright sites. They noted, however, that 
there may be another direct mechanism for the creation of the dark reacted site in order to 
account for the spatial distributions of the observed sites. Since in the present case, the 
sample was exposed to oxygen while held at 440°C, it is reasonable to assume that similar 
oxidation kinetics are occurring.

Figures 4.2(a) and 4.2(b) show two examples of a Si(111) surface exposed to 6.0 L 
of O\textsubscript{2} at 540°C. Figure 4.2(a) is typical of most of the surface. It shows reacted sites similar 
in appearance to those seen at lower temperatures, and a sticking coefficient \( s_o^d \approx 9 \times 10^{-3} \). 
Figure 4.2(b), on the other hand, shows something not seen at lower temperature: a true 
topographical hole in the surface \(~100 \text{ Å} \) across and 1 ML (3.1 Å) deep. Although the 
resolution in this image is not very high, a faint pattern of Si adatoms can be seen on the 
bottom of the hole. Under these oxidation conditions (\( T_s = 540°C \), \( P_{\infty} \approx 6 \times 10^{-8} \text{ torr} \), \( D_{\infty} = 6.0 \text{ L} \)) we find that such holes are widely spaced (\( \approx 5000 \text{ Å} \)) but are not uncommon. These 
holes give the first indication that oxygen-induced etching of surface Si atoms occurs for 
\( T_s \geq 540°C \).

Figures 4.3 and 4.4 show examples of Si(111) surfaces exposed to O\textsubscript{2} at 640°C at 
pressures of 5x10\textsuperscript{-8} Torr and 3x10\textsuperscript{-7} torr, respectively. Figure 4.3(a) is typical of most of the 
surface area after oxidation at the lower pressure. Flat terraces on these samples show
surprisingly low defect levels, even after O₂ exposures as high as 10 - 30 L. For example, the number of defects seen on the flat terrace of Fig. 4.3(a) implies a value \( s_0' \approx 1.2 \times 10^{-3} \) at 640°C, more than an order of magnitude smaller than that measured at 440°C.

Although the oxygen-induced defect density on the flat terraces is small, the behavior of the surface near step edges indicates that substantial oxidation effects have actually taken place. Surface steps are (in general) found to be much more irregular and "ragged" following 640°C oxidation than they were before. Furthermore, the lower surface near a step is often found in a metastable structure other than the stable 7x7 reconstruction. For example, the middle terrace in Fig. 4.3(b) shows three separate regions reconstructed into the 5x5 structure, several areas of 7x7, and even ~ 12 units cells of the 9x9 structure. We have only observed the non-standard 5x5 and 9x9 structures after oxidation at 640°C.

Figure 4.4 shows a typical surface area after 640°C oxidation at the higher pressure \( P_{ox} \approx 3 \times 10^{-7} \) Torr. This surface shows a much higher oxygen-induced defect density than seen at lower pressure, primarily in the form of many small depressions in the surface. Many (but not all) of the depressions have a measured (minimum) depth of 2-3 Å, and probably represent true holes in the surface. Since the STM tip may not be sharp enough to probe the deepest part of the hole, only a minimum depth may be concluded. Three larger holes can also be seen, each 1 ML (3.1 Å) deep. A quasi-ordered arrangement of Si adatoms is clearly evident on the bottom of the largest hole, showing a small region of the 5x5 structure and a single unit cell of the 9x9 structure.

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4.1.2 Mobile Vacancy Model

The monolayer-deep holes seen in Figs. 4.2(b) and 4.4 give direct evidence that surface Si atoms are etched by O₂ exposure in the temperature range 540°C - 640°C. Furthermore, the low defect density shown in Figs. 4.3(a) - 4.3(c) suggests that very little oxygen is left on the surface after 640°C oxidation at Pₓ ≈ 5x10⁻⁸ torr. We would like to understand these observations in terms of oxidation processes discussed in Chapter 1.

The most probable explanation for the observed behavior is that Si atoms are etched via the well-known process, O₂(g) + 2Si(s) → 2SiO(g). As discussed in Chapter 1, gas-phase oxygen adsorbs and reacts with silicon to produce (volatile) SiO, which can leave the surface via thermally activated desorption. This process is well characterized at higher temperatures (750-1150°C), although few quantitative studies have been done in the temperature range of our experiments. Again, the reader can refer to Fig. 1.9 which summarizes this high temperature behavior. The solid and dashed lines in Fig. 1.9 show the experimentally determined "critical conditions" for the growth of bulk SiO₂ on Si. For O₂ pressures below the solid line in the figure, the maximum desorption rate of SiO is fast enough that all the oxygen on the surface eventually desorbs in the form of SiO. This leaves an etched, oxygen-free surface. At O₂ pressures above the critical line, oxygen adsorbs fast enough for the eventual growth of a bulk SiO₂ film.

As introduced in section 1.3.3 and as previously discussed, we can account for many of our observations by simply assuming that Si atoms are etched via the desorption of SiO. In the simplest model, desorption of SiO at low O₂ pressure creates random Si vacancies on...
the surface. Because the surface temperature is high, these vacancies are likely to be mobile. In fact, a recent STM study of ion sputtering by Bedrossian and Klitsner\textsuperscript{83} indicates that sputter-induced vacancies on the Si(111) 7x7 surface are quite mobile for $T_s > 400^\circ$C. At elevated temperatures, these vacancies tend to coalesce into monolayer-deep depressions or diffuse to existing step edges and cause step retraction.\textsuperscript{83} A schematic of this process is shown in Fig. 4.5. The step edges seen after high-temperature sputtering (especially those surrounding large coalesced depressions) appear to be more ragged than the original steps on the surface.

We expect that Si vacancies created by SiO desorption should show behavior similar to those created by ion sputtering. Vacancy coalescence would produce the monolayer-deep holes seen in our experiments, as well as the ragged step edges. Furthermore, "new" surface material should be exposed on the bottom of holes and at the lower surface of a retracting step.\textsuperscript{83} Initially, this newly exposed material would not exhibit the 7x7 structure, but in the temperature range 540-640°C it is well known that disordered\textsuperscript{33} or cleaved\textsuperscript{20} Si(111) surfaces can transform into the metastable 5x5 and 9x9 structures as well as the (stable) 7x7 structure. It is reasonable to assume that some of the new surfaces exposed by oxidation-induced etching might also form into the 5x5 or 9x9 structures as shown in Figs. 4.3, 4.4, and 4.6(a). Some of the newly exposed surfaces could stay disordered, however, and an example of this is shown in Fig. 4.6(b).

These elevated temperature Si(111) oxidation findings were presented in Ref. 90 and were similar to an independent study by Feltz \textit{et al.}\textsuperscript{76} which appeared in print a few months before our article. Although both studies examined Si(111) oxidation under similar
conditions, the studies did have slightly different emphasis. Feltz and coworkers did not address the issue of metastable reconstructions forming on the freshly exposed surfaces. They did, however, present a mobile vacancy model similar to the one presented here. In addition they went on to note that the oxidation-induced etching around 680°C was observed to be of the step-flow variety (i.e. the vacancies migrated to steps where they caused the step to retract) for the first monolayer of silicon removal, but then proceeded by the growth of vacancy islands within a terrace. These authors postulated that this transition from step-flow to vacancy island nucleation within a terrace was due to the disordered nature of the freshly exposed surface after the first monolayer was removed. They believed that this defective surface enhanced vacancy island nucleation. Feltz et al. continued these studies on Si(111) while we shifted our focus to the more technologically relevant Si(001) surface. Further discussion of their subsequent work of will be presented with our Si(001) studies in section 4.2.

4.2 Si(001)-(2x1)

4.2.1 Preferential etching

As mentioned in the previous section and introduced in section 1.3.5, Bedrossian and Klitsner postulated a mobile vacancy model based on their ion sputtering studies of Si(111). This group continued these studies on Si(001) where they showed that diffusing vacancies created by ion-sputtering at $T_s \geq 450°C$ preferentially terminated at
B-type steps. This phenomenon was analogous to the preferential attachment of diffusing silicon adatoms to B-type steps during homoepitaxial, step-flow growth. Furthermore, it was found that if 0.5 ML of silicon was removed under step-flow etching conditions that an essentially single A-domain surface would result (because most of the B-type terraces were removed by the preferential etching). Similarly, Hoeven et al. showed that an essentially single B-domain surface could be created by growing 0.5 ML of silicon.

As a side note of technological relevance, the single domain surface may be a preferred substrate for subsequent growth of bilayered materials such as GaAs. With GaAs growth, one complete layer of As forms then one complete layer of Ga forms over it. This being the case, step bunches of even numbers of accumulated single steps (which would result from a single domain surface) are desirable so that antiphase boundaries can be avoided. With odd numbers of single steps, the As layer on the upper terrace would align with a Ga layer from the lower terrace forming an undesirable boundary.

The reason for the preferential attachment of adatoms or vacancies to the B-type steps is still somewhat controversial. Most research suggests that anisotropic accommodation coefficients (i.e. sticking coefficients or kinetically speaking, attachment barriers) are responsible and required, but that anisotropic diffusion may also play a role. Since these structures are formed during elevated temperature processes the added complexity of whether these kinetic effects or energetic effects are dominating is also present. For example, with vacancy islands or growth islands, the relative lower energy of the $S_A$ step as discussed in the introduction would suggest that both types of islands be
elongated along the direction which maximizes the number of $S_A$ step segments, and this is in fact observed experimentally. The reduction of the $S_A:S_B$ ratio for Si epitaxial islands during annealing experiments, however, suggests that at least some kinetic factors must also be playing a role during the original island formation. Since anisotropic sticking at $S_B$ steps during epitaxial growth or vacancy termination at the end of a vacancy island (i.e. the kinetic aspects) would result in the same preference for elongated islands, it seems most likely that a combination of step energetics as well as the kinetic effects are both contributing to the observed effects.

Knowing these ion sputtering results on Si(001), we performed experiments to try to reproduce the single domain structure observed by Bedrossian and Klitsner by using oxidation-induced etching. For low oxygen pressures and doses at 640°C, we found that the oxidation-induced etching does in fact also preferentially etch B-type steps over A-type. Figure 4.7(a) shows a clean starting surface with well defined, evenly spaced A and B-type steps, while Fig. 4.7(b) shows a different area of the surface after exposure to 50 L of $O_2$ at $2\times10^4$ torr and 640°C. Figure 4.7(c) shows that oxidation-induced etching at $2\times10^4$ torr and 640°C also leads to clear, preferential retraction of B-type steps. In contrast to sputter-etching, however, the formation of long step fingers (primarily on B-type steps) prevents the formation of a single A-domain surface. As the dose becomes higher, etching becomes prevalent at B-type kinks on A-type steps, causing the local step orientation to randomize. At this point steps have a large degree of mixed A and B-type character, and hence both types of terraces become equally etched, and a single A-domain
is not achieved. The reason for creation of these fingers during oxidation-induced etching and not during sputter-induced etching will be discussed in the following section.

To quantify this preferential etching behavior, we have measured the relative areas of A-type terraces (above an A-type step) and B-type terraces (above a B-type step). A terrace is assigned to be A-type (B-type) if its dimer rows run perpendicular (parallel) to the original [110] sample miscut direction. The ratio of A-terrace areas to B-terrace areas as a function of dose is shown in Fig. 4.7(d). The A:B ratio is observed to increase from a value near one with increasing dose (indicating preferential retraction of B-type steps) up to doses in the range of 30 - 50 L. Thereafter, the A:B ratio decreased for higher doses as the step directions randomized. Below we show that these step fingers and subsequent step direction randomization are caused by nm-sized oxide clusters which pin the steps during etching.

4.2.2 The pinning mechanism

Upon close examination of the fingers observed during oxidation-induced etching, it is clear that almost every finger has a distinct defect toward the end of the structure which seems to be preventing the surface from etching. It is a fairly well known phenomenon that certain types of localized contamination can prevent steps from etching. As originally suggested by Price, Vermilyea, and Webb, a pinning site during step retraction will first form a long finger, but as step retraction proceeds the end of the finger will eventually break away to form a monolayer-high island.119 As subsequent steps pass
by the pinning site, the island will progressively increase in relative height (since the substrate is being etched lower), eventually leading to the formation of a three-dimensional etch structure. This pinning mechanism is shown schematically in Fig. 4.8.

We now relate this pinning mechanism to the observation of finger and island formation on Si(001)-(2x1). Figure 4.9 shows several images which reveal that in almost every case the ends of the step fingers and the Si islands are associated with a characteristic defect structure, which often appears as a dark, roughly linear structure oriented perpendicular to the dimer-row direction (Fig. 4.9). This suggests that the fingers and Si islands are both caused by local pinning of the step edges by the defect as the steps retract during oxidation-induced etching. As a retracting step reaches a pinning site, a long finger is first formed (such as that marked in Fig. 4.9(a)). As step retraction proceeds, the end of the finger can break away leaving a small island centered on the pinning site, as shown in Fig. 4.9(b). This pinned island can then pin the next step that reaches it, producing an island at the end of a finger (Figs. 4.9(a-inset) - 4.9(c)), and finally an island on an island (circled in Fig. 4.9(c)) as this second finger breaks away. Fig. 4.9(c) also shows that multiple pinning sites can produce much larger break-away islands. We note that the observation of multi-level islands a few layers high is qualitatively consistent with the 1 to 3 ML of Si etching estimated for these oxidation conditions, $D_{ox} = 63 \text{ L}$, $P_{ox} \approx 4 \times 10^{-4} \text{ torr}$, and $T_s = 640^\circ C$ (see section 4.2.3). We also note that analogous step pinning behavior was reported by Donig et al. during oxidation of Si(111).

The actual mechanism by which a material prevents etching is somewhat uncertain. In the case of a chemically reacted species, for example, the resulting complex
may simply be more stable than the bare silicon at the reaction temperature. The greater stability may come from such properties as a very high diffusion barrier or a very high desorption barrier due to large bond strengths. In contrast, it is known that silicon dimers (in groups of 2, i.e. a four-pack of Si atoms) can attach and break-away from a b-type step with relative ease even at temperatures around 400°C. In addition, the structural nature of the reaction product may introduce local strain fields which could also inhibit etching of the underlying silicon. Whatever the cause(s), we find that these characteristic sites can at least inhibit steps from etching.

Another outstanding question is: How large does a pinning site have to be before it can actually fully prevent a step or bunches of steps from being etched back further? The answer to this question most likely depends on a number of factors, but sites as small a few atoms in lateral size have been observed to modify a single step’s retraction. Larger step bunches are generally prevented from etching by laterally larger pinning sites, suggesting that the pinning sites are also growing (vertically and laterally) in time. This size issue will be discussed in greater depth in section 4.5.

Finally, we note that the pinning mechanism discussed here for Si(001) also applies to Si(111) surfaces. Our studies and others’ have shown that at higher doses distinct pinning sites are evident on 7x7 surfaces. Since the early work presented in section 4.1 was at very low doses, distinct pinning sites were not observed. After clearly seeing this mechanism on Si(001)-(2x1) surfaces, however, further studies under similar conditions showed that the same behavior was in fact observed for the Si(111)-(7x7) surfaces as well. These results are reported in sections 4.4 and 4.5.
4.2.3 Pinning Site Identification - Nucleated Oxide Clusters

The next question concerns the nature and origin of the pinning sites themselves. A telling indication of the origin of these sites can be seen in the low-dose, pressure-dependent oxidations shown in Fig. 4.10. Figure 4.10(a) shows a 300 nm x 300 nm scan after surface cleaning. The clean surface has a typical starting defect density < 2%. Figures 4.10(b) - 4.10(f) show scans of the same size as 4.10(a) after oxidation at $P_{ox} = 2.1 \times 10^4$, $4.1 \times 10^4$, $6.0 \times 10^4$, $8.0 \times 10^4$, and $1.0 \times 10^5$ torr respectively, all with the same total $O_2$ dose of 63 L (1 L = $1 \times 10^5$ torr-s exposure) and all exposed at 640°C. Since the same total exposure was desired, it should be noted that varying the pressure required changing the duration of oxygen exposure. Thus, for example the oxidation at $8.0 \times 10^4$ torr required only about half the time as the oxidation at $4.1 \times 10^4$ torr required. Samples were thermally cleaned before each oxidation, and all had roughly the same initial step structure and defect density.

At $P_{ox} = 2.1 \times 10^4$ torr (Fig. 4.10(b)) long fingers are seen extending from surface steps, and in many cases small (< 5 nm) Si islands with pinning defects are found at the ends of the fingers (these appear as small white spots in Fig. 4.10(b)). The number of fingers and Si islands (or equivalently pinning sites) increases at $P_{ox} = 4.1 \times 10^4$ torr (Fig. 4.10(c)), and again at $P_{ox} = 6.0 \times 10^4$ torr (Fig. 4.10(d)), where a number of larger "break-away" islands (see discussion of pinning mechanism above) start to be found. The trend continues for $P_{ox} = 8.0 \times 10^4$ torr (Fig. 4.10(e)), and when $P_{ox} = 1.0 \times 10^5$ torr (Fig. 4.10(f)) the original step structure can no longer be distinguished, and the entire surface has become covered with small pinned islands.
The image in Fig. 4.11 is a close-up of Fig. 4.10(f) and shows that this heavily terraced surface is composed of a mixture of relatively clean 2x1 areas side by side with extended areas covered by disordered and quasi-ordered arrangements of bumps and depressions. We note that some of these quasi-ordered structures (marked by arrows) appear similar to oxide structures observed by Udagawa, Niwa, and Sumita following 600°C oxidation of Si(100)-2x1 at a higher pressure (≈ 1x10⁻⁶ torr). This suggests that for the conditions shown in Figs. 4.10(f) and 4.11 oxide growth is becoming comparable to surface etching and that many oxide nuclei have already started to grow into extended oxidized regions.

This strong pressure dependence of the step pinning density and the continuous transition into an oxidized surface for P ≥ 1x10⁻⁷ torr suggests that the pinning sites are directly connected to oxygen, i.e., they represent small oxidized regions which have nucleated on the surface. This is same conclusion that Donig et al. came to for the pinning sites they observed after oxidation of Si(111) under similar conditions. In fact Feltz et al. showed with Auger Electron Spectroscopy (AES) that oxygen was in fact present on the surface after oxidation under these same conditions and concluded that since the surface area between the pinning sites was clean that the pinning sites themselves contained oxygen. These results are also consistent with predictions based on an extrapolation of past measurements of the "critical conditions" for oxide growth on Si which indicate that at 640°C the critical pressure for oxide growth should be ~1x10⁻⁹ torr. From this one would expect an oxide film to eventually form even at the lowest oxidation pressures used in our experiments. We also note that the pinning defects are typically 25-50 Å long, 7-20 Å
wide, and in some cases (as in Fig. 4.9(a)) are found to have a measured depth of as much
as 4 Å (~3 ML) in constant-current STM images at -2 V sample bias. Such a "deep" defect
is consistent with an oxidized region (with a reduced density of states near the Fermi level)
which may extend several layers down as seen with room temperature oxidation.

One other possibility is that they are simply due to contamination present on the
surface before oxidation. However, the results shown in Fig. 4.10 would appear to rule this
out since all scans were taken after the same total oxygen dose, and hence approximately
the same total amount of Si etching. We note that reported initial sticking coefficients for O₂
on Si(001) are usually in the range $s_0 \approx 0.02$ to 0.05 around 600°C, so a dose of 63 L
corresponds to reaction of roughly 1 to 3 ML of Si atoms. High resolution images reveal
that most of the surface shows the 2x1 structure with a relatively low defect density
(particularly for $P_{\text{ox}} \leq 6 \times 10^{-4}$ torr), indicating that the amount of aggregated oxygen is « 1
ML. Hence, surface etching dominates oxide growth for the oxidations shown in Fig. 4.10,
and roughly 1 - 3 ML of Si have been etched. If contaminants were the sole cause of
pinning, one would expect to see roughly the same pinning density and step structure for all
oxidation pressures since the same amount of material has been etched away in each scan,
thus exposing the same number of pinning sites. This is clearly not the case, so surface
contaminants by themselves cannot be the cause of the pinning. We can not rule out,
however, that contaminants may help to nucleate stable oxygen-related sites.

Further support that these pinning sites are oxide clusters and not contaminants is
evident from their numbers at elevated temperatures. We note that the pinning densities
seen in Fig. 4.10 are not significantly affected by a ~30 min anneal at 640°C, but are
reduced by a factor of 2 and 10 following a 3 min anneal at 740°C and 840°C, respectively. If these sites were related to a common contaminant such as carbon, we would not expect their numbers to decrease at temperatures as low as 740°C since carbides are stable to much higher temperatures (950-1050°C). Silicon monoxide, however, desorbs at lower temperatures and is therefore consistent with these annealing results.

As further support to the fact that pinning site densities were not being affected by starting surface defects, the "pre-etch procedure" originally discussed in section 2.5 should be recalled. There it was found that oxidation at 940°C and 6×10^{-8} torr resulted only in surface etching and that no pinning sites were observed. This indicates that the species responsible for pinning the surface is volatile at 940°C. This again is consistent with SiO desorption, but somewhat unlikely for carbide species. It has been found that to reliably rid the surface of carbon related defects during the flash procedure, temperatures should be taken to \( \sim 1250°C \) where it is believed that the carbon diffuses into the bulk. We thus conclude that carbides are not responsible for the pinning we observe.

This pre-etch procedure also removes the top 2-3 layers of silicon so any surface species adsorbed between oxidation runs will be removed by the etch. Again, this helps to minimize any effects that surface defects resulting from gas-phase adsorbates between experiments may have. Such an effect may be on the sticking coefficient for the oxygen on the surface as discussed in section 4.4.4.

Other support for identifying these sites as oxide clusters comes from the work of others. Smith and Ghidini\(^\text{18}\) have previously reported that \( \mu \text{m-sized} \) conical structures
could form at high temperatures (> 1000°C) and high doses, provided the sample
temperature and O₂ pressure were within a narrow transition region between the active
and passive oxidation regimes. They postulated that these structures were Si cones
covered with a thin SiO₂ layer, formed from a tiny oxide nucleus which grew down the
sides of the cone as the surrounding surface was etched away (Fig. 1.10).

We propose that the nanometer-sized conical islands observed in our high dose
experiments (Fig. 4.12) may in fact represent an early stage of the larger structures
reported by Smith and Ghidini. The smaller structures in our case are formed in a
corresponding transition region between passive and active oxidation regimes, but at
much lower temperature and O₂ pressure. In support of this connection, we note that the
STM tunnel current often becomes unstable at low tunnel voltages when the tip was
located over an island, but could generally be stabilized by raising the tunnel voltage
above a few volts. This is consistent with the expected behavior if a thin layer of SiO₂
covers the island because SiO₂ has a larger bandgap than bulk silicon.

Further studies were conducted on these high dose etch structures. An HF dip
was used (ex-situ) to remove any oxygen that was on the surface, and the same sample
that had been characterized with STM was placed in an air AFM and examined. It was
found that no substantial change in the heights of the etch structures were observed. This
is consistent with the findings for Smith and Ghidini’s etch structures and is consistent
with the atomic-scale appearance of the “conical islands” which seems to be primarily
silicon terraces shaped into the form of a ziggurat with an oxygen-related disordered area
at the apex. Although some of oxide may be present along the sides of the island
structure, it should be noted that it is still possible to see silicon dimers on some of the island’s terraces as seen in Fig. 4.12.

Below is a summary supporting the identification of pinning sites as oxide clusters.

- pinning density is sensitively dependent on oxidation pressure
- oxidation conditions should produce some stable oxide as indicated by critical curves and the areas between pinning sites are generally quite clean (i.e. no evidence of O₂)
- tunnel current is frequently unstable over clusters unless higher bias voltages are used, consistent with an insulating material with a larger band gap than silicon
- pinning sites show a decrease in density upon annealing at moderate temperatures as might be expected from oxide cluster break-up and SiO desorption
- exposure at the same oxygen pressure, but higher temperature (940°C) shows no evidence of pinning, only etching
- pinning sites at higher doses have larger lateral sizes consistent with an oxide cluster which is growing in time.
- independent AES measurements detect the presence of O₂ under similar conditions.

4.3 Pinning Sites to Oxide Nucleation Theory

At this point it was realized that quantitative information regarding oxide nucleation kinetics could be obtained by counting the pinning sites. If indeed the pinning defects are small oxide nuclei, then we should be able to investigate how the nucleation
process depends on pressure and temperature by directly counting pinning sites as a function of these variables. The assumption made here is that each pinning site corresponds to a single nucleated oxide cluster, and for the remainder of this document, these pinning sites will simply be referred to as oxide clusters. This novel approach for investigating oxide cluster nucleation kinetics is only possible due to the simultaneous etching and nucleation that exposure to oxygen in the transition regime provides. Without concurrent etching, nucleated oxide clusters are difficult to identify and count. The fact that clusters mask against etching, however, makes clusters readily countable when the surrounding substrate is being etched away. It is advantageous then to focus one’s studies on higher doses and thus minimize counting uncertainties.

In the sections 4.4 and 4.5 oxide cluster densities and cluster shapes and sizes will be reported as functions of oxidation pressure, $P_o$, silicon substrate temperature, $T_s$, and dose, $D_o$. The experimental observations will simply be stated here, and the analysis will follow in Chapter 5. Higher doses, in which many layers (5-50) of etching has taken place, will be the primary focus. By performing this analysis, atomic-scale models for oxide nucleation and growth will be directly tested and discussed in Chapter 5. We also note here, that the analysis of cluster densities that follows is for both Si(001)-(2x1) and Si(111)-(7x7), since we have found that the extended dose behavior of Si(111) is similar to that of Si(001) in terms of the pinning mechanism and cluster counting possibilities.
4.4 Oxide Cluster Density

4.4.1 Dose Dependence - High Dose Saturation

Here we address the dose dependence of the oxide cluster nucleation. Figure 4.13(a)-(d) shows 300 nm x 300 nm scans of four oxidations done at the same temperature (690°C) and O₂ pressure (6x10⁻⁸ torr), and for a total O₂ doses of 100, 200, 400 and 800 L respectively on Si(001). Clearly the number of oxide clusters has increased from 4.13(a) to 4.13(c). However, doubling the exposure from 400 to 800 L results in approximately the same number of clusters on the surface (77 in each of Figs. 4.13(c) and 4.13(d). This indicates that at high doses the oxide cluster density saturates. Close-up scans of the areas between the islands (shown in Fig. 4.14) indicates that the 2x1 dimer reconstruction is still intact and is not covered with an oxide layer even for relatively high doses (in this case 800 L). We believe that the larger defect density seen in the extended dose images is due to the appreciable amount of residual oxygen that adsorbs on the surface during the cool-down of the sample. Extended doses of oxygen simply take the ion pump longer to remove from the chamber and hence increase the chance of significant lower temperature oxygen adsorption during sample cooling.
4.4.2 Pressure Dependence

The low dose (63 L) pressure dependence has been previously presented as support for the identification of pinning sites as oxide clusters (Fig 4.10). Figure 4.15(a) shows the results of counting the nucleated oxide clusters of Fig. 4.10. In Fig. 4.15(b) we plot the corresponding oxide nucleation rate $J_{\text{ox}}$ (i.e., density of oxide clusters divided by exposure time) vs oxygen pressure $P_{\text{ox}}$ for sample conditions shown in Figs. 4.10(c)-4.10(f). On this log-log plot, the data points are best fit by a line of slope 2.4, but at lower pressures are also in reasonable agreement with a line of slope 2.

These findings suggest that oxide cluster nucleation is at least second order in oxygen pressure. This implies that at least 2 oxygen species are required to nucleate a stable oxide cluster. One species by itself or even one oxygen species plus a defect would not explain the second ($+$) order dependence. The ramifications of this fact on atomic-scale modeling will be discussed in Chapter 5.

In the high dose (saturation) regime we find distinct pressure dependence as well. Figure 4.16(a) shows how the saturation level for oxide cluster densities is affected by $P_{\text{ox}}$ on Si(001) and in Fig 4.16 (b) for Si(111). For these data samples were all oxidized at 690°C. Intuitively, higher oxygen pressures result in larger oxide cluster densities consistent with the idea that more nucleating oxygen species are on the surface at any given time.
4.4.3 Temperature Dependence

We next address the temperature dependence of the initial oxide cluster nucleation rate $J_{ar}$. Figures 4.17(a) and 4.17(b) show top-view gray scale images of two different 500 nm x 500 nm areas of a sample which had a ~50°C temperature gradient across it during oxidation at $P_{ar} \approx 6 \times 10^{-4}$ torr and $D_{ar} \approx 150$ L. Since these measurements were both made following a single oxidation, they permit us to directly monitor the temperature dependence of $J_{ar}$ with all other experimental variables (e.g. $P_{ar}, D_{ar},$ initial surface defect density, miscut, etc.) held fixed. The number of oxide clusters is clearly greater at the low temperature side of the sample. Figure 4.17(c) shows an Arrhenius plot of $J_{ar}$, determined by counting oxide clusters at different positions across the sample and dividing by the oxidation time. The data show approximate Arrhenius behavior over this temperature range. The solid curve shows the best-fit line, with a slope indicating an effective activation energy of -3.6 eV. As we discuss below, this temperature dependence is not due to a single thermally activated process with a negative energy (which is unphysical), but rather results from a combination of thermally activated processes (including desorption, diffusion, nucleation, etc.). The dashed curve shows the dual-species model prediction which will be discussed in Chapter 5. Many such experiments have been done at doses ranging from 50 to 800 L over a similar temperature range, and in all cases the resulting effective activation energies were between -3.3 and -4.0 eV. We also made measurements on uniformly heated samples oxidized at different temperatures.
In these cases, $J_{\text{abs}}$ was roughly constant across an individual sample, with the best-fit effective activation energy in the same range.

Temperature dependence was also examined in the high dose regime. These data are shown in Fig. 4.18 (a) for Si(001) and Fig. 4.18 (b) for Si(111). As for the pressure dependence, the intuitive result (based on traditional nucleation and growth theory as discussed in Chapter 5) is again observed. Higher temperatures result in a lower island density (i.e. fewer nucleated oxide clusters). The reason here is that at higher temperatures more oxygen desorbs reducing the oxygen monomer density and hence reducing the density of nucleated clusters. In addition, at higher temperatures the nucleating species may diffuse longer distances so they can sample larger areas and hence have a greater probability to find an existing cluster and attach than to nucleate a new one. Thus it is a complex interplay nucleation, growth, diffusion and desorption activation energies which dictates the resulting effective temperature dependent behavior.

### 4.4.4 Initial Defect Density Dependence

We have found that there is some degree of variation in cluster density counting when starting with surfaces that had different initial defect densities. Fig. 4.19 shows the difference between oxidation experiments done under the same temperature-pressure conditions, but with different starting defect densities for the silicon surfaces. There is clearly evidence here that defects do lead to more nucleated oxide clusters. It is important to note, however, that the mechanism by which this occurs is unclear. For
example, the defects may serve as enhanced nucleation sites or they may serve simply as enhanced adsorption sites. Enhanced adsorption would be equivalent to increasing the sticking coefficient which in turn is equivalent to increasing the pressure. However, it should be noted that if we assume the defects only occur in the first atomic layer and are removed by the etching process, then after that layer is etched, the sticking coefficient might drop back to a value which is similar for all types of extended dose (>1 ML etched) oxidations. The problem here is that the true nature of the defects is unknown and their susceptibility to removal by etching is unknown as well. Enhanced sticking is actually quite likely, based on the previous measurements (see section 1.3) which show that initial oxidation occurs preferentially at defect sites on Si(001) and at dangling bonds on the Si(111) surface.

For the quantitative measurements involving cluster counting, defect densities were minimized by flashing the sample numerous times before accumulating counting statistics. In this way the system became progressively cleaner as successive heating of the sample desorbed impurities (which we believe can create defects on the sample during the flash) from the surrounding sample holder, thus reducing the defect density observed after a flash. Qualitatively, this slow purging of the system was evident from the falling maximum system pressure observed during subsequent sample flashes (especially initially). We estimate that after the sample was flashed 3-4 times, the system was clean enough to get fairly reproducible initial surface defect densities (~2%) which in turn would result in oxide cluster densities that varied well within a factor of two from each other for a given set of oxidation conditions.
4.4.5 Miscut Dependence

Like a higher defect density, larger miscut introduces many steps on the surface, each of which can actually be thought of as a type of surface defect. Atomic steps can be considered defects because they have reduced bonding coordination as compared with terrace atoms. This being the case and noting the enhanced sticking seen at defects, it seems reasonable that there may be higher sticking on samples with a higher miscut (i.e. those with more steps). One difference with step defects as opposed to the initial starting defect density, however, is that the long range step density is set by the miscut and hence is constant (over long length scales) during the course of an oxidation. This being the case, enhanced sticking should extend throughout the course of an oxidation and not just during the first monolayer of etching as with the initial surface defects discussed in the previous section.

Our experiments have shown that high miscut samples do in fact nucleate more oxide clusters (Fig. 4.20(a)). Again a question arises as to which role the increased step density plays, enhanced sticking, enhanced nucleation, or both. A better measurement to address this question will be discussed in section 4.5.1. There it will be shown that since etching is the dominant reaction seen throughout our experiments, that the height of the clusters will really indicate most effectively how much oxygen has actually reacted with the silicon surface. In fact, it will be shown that this height analysis seems to be consistent with an increased sticking coefficient.
We note here that Wurm et al.\textsuperscript{10} have used low energy electron microscopy (LEEM) to study oxidation-induced etching under similar conditions, but on Si(001) samples with much lower miscut angle. On large terraces, they observed preferential etching in a direction parallel to the dimer rows, behavior consistent with the preferential retraction of B-type steps reported here. One difference, however, is that their LEEM measurements did not indicate substantial step pinning at 600°C even at O\textsubscript{2} pressures as high as 5x10\textsuperscript{-4} torr.

A possibility is that the lower lateral resolution of the LEEM apparatus (≈ 15 nm) may have missed the smaller islands we observed for D\textsubscript{ox} ≤ 100 L (see Fig. 2(a)). Recent STM work\textsuperscript{18} by this group at these same conditions did in fact show pinning similar to that observed in this study, but at a much lower density. We also note that Wurm et al.\textsuperscript{10} observed a sticking coefficient that was ≈8 times smaller than ours. A possible cause for this difference in the sticking coefficient may in fact be due to differences in sample miscut or may also be due to different amounts of background water vapor (which can greatly enhance silicon oxidation\textsuperscript{17}) or even a difference in O\textsubscript{2} ionization levels. Whatever the cause, it is important to note that the nucleation rate should scale as the square of the sticking coefficient at a given temperature, pressure, and dose as discussed in Chapter 5. This follows because the model predicts that the oxide cluster nucleation rate varies quadratically with the rate that oxygen actually reacts with the surface, which is proportional to the product s times P\textsubscript{ox}. Hence, the lower sticking coefficient in the experiments of Wurm et al. should result in a factor of ≈64 lower pinning density and a
factor of ~8 less etching than observed in our study for oxidation at the same temperature, pressure, and dose.

4.5 Oxide Cluster Size and Consequences

4.5.1 Height Evolution with Dose: The constant etch rate

If we return to the dose dependent data shown in Fig. 4.13, and examine the height of the clusters we find an interesting result. The data from Fig. 4.13 are also plotted as 3D rendered surfaces. Here it is apparent that although the number of clusters saturates, the height of the clusters continues to increase even at high doses. In fact, the height of the clusters at 800 L has increased to roughly twice the height at 400 L. We find that the average cluster height increases linearly with dose (Fig 4.21), indicating that the vertical etch rate $\eta$ remains roughly constant on the clean terrace areas between the clusters. Note that the vertical scale (-20 $\rightarrow$ 50 Å) in the perspective views has been greatly expanded relative to the horizontal scale to enhance island visibility.

As can also be seen from Fig. 4.21, the vertical etch rate is very much dependent on the oxidation pressure. Higher oxidation pressures result in faster vertical etching since more oxygen is reacting with the silicon surface per unit time. Since the reacted flux, $F$, is just proportional to the oxidation pressure, $P_{ox}$, times the sticking coefficient, $S_g$, it is clear that a similar increase in the vertical etch rate, $\eta$, would be seen if the sticking coefficient goes up as well.
Finally, a word about the algorithm for determining cluster heights should be noted. For each image the best-fit, least-squares paraboloid was subtracted from the data to remove sample tilt and second order nonlinearities in the piezo scanner. Then the user would mark sections of the original base plane. Another routine would then fit the best plane to these points, and this plane would be subtracted from the data. In principle this routine essentially allows for the user to subsequently go in and "read-off" the heights of the islands in the image. From this linear increase in the average island height, we may deduce that the vertical etch rate is approximately constant for the clean areas between the clusters.

4.5.2 The Sticking Coefficient

The fact that the vertical etch rate is constant and the fact that the total amount of silicon removed as SiO is much greater than the amount of oxygen left on the surface enables us to make a very good approximation to the total amount of oxygen that has reacted with the surface. Since the oxidation pressure is known and we can measure the reacted amount of oxygen from the amount of removed silicon, we can obtain a measure for the sticking (or reaction) coefficient of oxygen on the silicon surface.

First we recall from classical gas kinetics that the flux, $\Phi$, of gas molecules impinging upon a surface is given by:

$$\Phi = \frac{P}{\sqrt{2\pi mk_b T}}$$
where $P$ is the average gas pressure measured in Pascal, $m$ is the mass of a gas particle (in our case $m_{\text{O}_2} = 5.34 \times 10^{-26}$ kg), $k_B$ is Boltzmann's factor ($1.38 \times 10^{-23}$ J/K), and $T$ is the gas temperature (300 K). This gives the flux in units of number of particles per $m^2$ per second. By comparing the measured reacted flux, $F$, with the impinging flux, $\Phi$, we can see what fraction of impinging flux actually reacted with the silicon. This measure of the sticking coefficient is summarized in Table 1 for various oxidation conditions. It should be noted that the flux is normalized to a scan size of 5000 Å x 5000 Å which is unnecessary, but nevertheless provides an intuitive feel for the actual quantity of oxygen molecules reacting with the silicon surface on the size scale of typical scans. This being the case, the reactive flux, $F$, per scan is calculated by multiplying the etch rate by the number of sites per monolayer per scan. Si(001) has $1.695 \times 10^6$ sites per monolayer (ML) per scan and Si(111) has $3.915 \times 10^6$ sites per bilayer (BL) per scan. The impinging flux, $\Phi$, is calculated from $P_\alpha$ and the equation above and is also normalized to a scan size. The sticking coefficients, then, are just the ratio of $F:\Phi$ and range from about 3% to 5% for the normal (low) miscut samples.

It should be noted that the variation in $s_o$ as a function of pressure may be somewhat misleading. In fact, we have no reason to believe that the sticking coefficient should be a function of pressure. Most likely this large variation in $s_o$ is due to the uncertainty in measuring the pressure. In fact, if an average sticking coefficient of 4.3% is assumed for all Si(001) (low miscut) samples, and the pressures are "back-calculated" from the etch rates, we see that the pressures become $1.4 \times 10^{-7}$ torr, $6.1 \times 10^{-8}$ torr, and
2.3x10^4 torr which are all well within the reported uncertainty (± 50%, see section 2.7) in measuring the pressure.

It should also be noted, however, that sticking coefficients have been traditionally reported over a range of values from 0.0002 to 0.20 for molecular oxygen with the silicon substrate. Reasons for the variations have been attributed primarily to trace backgrounds of water vapor which enhances the oxidation reaction and to different levels of O_2 ionization which can come from hot filaments such as an active ion gauge. Another reason cited has been enhanced dissociation at steps which would be consistent with our larger miscut results as discussed below. In addition, we may add to this list the fact that different starting defect densities affect sticking as well. Again, however, we believe that most of the variation in our sticking coefficients reported in Table 1 are due to uncertainties in the pressure measurements.

For high miscut samples, however, measured sticking coefficients were about twice as high as the low miscut sticking coefficients. This difference is beyond the variation we would expect from surface defects, background water, etc. In this case, it appears that step structure of the sample is causing the larger sticking coefficient. As was introduced in section 4.4.5, samples with higher step densities resulted in surfaces with a larger density of nucleated oxide clusters than those samples with lower miscut which were exposed to the same oxidation pressure, temperature, and dose. Here we show (in Table 1) that the measured etch rates are in fact greater as well. This being the case, we may conclude that the higher step density results in a higher sticking coefficient.
Table 1. Conversion table for pressure, etch rates, flux, and sticking coefficient.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$P_{ox}$ (torr)</th>
<th>Etch Rate</th>
<th>$F$ (#/scan/s)</th>
<th>$\Phi$ (#/scan/s)</th>
<th>$s_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(001)</td>
<td>1.2x10^{-7}</td>
<td>0.00333 ML/s</td>
<td>5640</td>
<td>107,000</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td>6.0x10^{-8}</td>
<td>0.00138 ML/s</td>
<td>2340</td>
<td>53,500</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>3.0x10^{-8}</td>
<td>0.000516 ML/s</td>
<td>875</td>
<td>26,800</td>
<td>0.033</td>
</tr>
<tr>
<td>Si(111)</td>
<td>1.2x10^{-7}</td>
<td>0.00142 BL/s</td>
<td>5560</td>
<td>107,000</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>6.0x10^{-8}</td>
<td>0.000722 BL/s</td>
<td>2830</td>
<td>53,500</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td>3.0x10^{-8}</td>
<td>0.000293 BL/s</td>
<td>1150</td>
<td>26,800</td>
<td>0.043</td>
</tr>
<tr>
<td>Si(001) high miscut</td>
<td>6.0x10^{-8}</td>
<td>0.00244 ML/s</td>
<td>4140</td>
<td>53,500</td>
<td>0.077</td>
</tr>
<tr>
<td></td>
<td>3.0x10^{-8}</td>
<td>0.00131 ML/s</td>
<td>2220</td>
<td>26,800</td>
<td>0.083</td>
</tr>
</tbody>
</table>

4.5.3 Lateral Size

The issue of determining the lateral size of an oxide cluster is somewhat complicated by the fact that the tip’s resolution can influence the measurement. One must constantly keep in mind that the sharp features on the sample’s surface essentially behave like a tip, and if the real tip is particularly dull, then the sample images the tip. In these cases oxide clusters may appear laterally much larger than they actually are. In this manner, island sizes may be a convolution of tip and cluster geometry, so accurate determination of the later size of a cluster is difficult. Furthermore, it is difficult to determine the boundaries of the oxidized region when examining images that are 500 x 500 nm. There is ambiguity even in close-up images due to the disordered nature of the oxide (see for example Fig. 4.12). To complicate matters oxidation is known to proceed in the vertical direction, so from the standpoint of determining a true coverage for the
surface, STM is insufficient and other methods such as XPS and AES should be used. Unfortunately these techniques were not available during the course of these experiments. Nevertheless, total oxygen coverage was estimated from the lateral sizes of oxide clusters and in all cases was less than about 10%.

4.5.4 Cone angle

Under much higher pressure-temperature conditions but in a similar transition regime between oxidation-induced etching and oxide nucleation, Smith and Ghidini showed that large (micron-sized), pyramid shaped etch structures resulted during oxidation. We do note, however, that the overall height-to-width aspect ratio of the cones observed here is substantially smaller than those observed by Smith and Ghidini. This may be because the intrinsic shape of the islands is a strong function of oxidation temperature and pressure, or because they have not grown large enough to reach their limiting shape, or even because the finite size of the STM tip causes the islands to appear wider than they actually are. It is also possible, however, that the different shape is due to a completely different physical origin. Interesting studies may involve the examination cone angles as a function of oxidation pressure over a much wider range of oxidation conditions.
Figure 4.1 Si(111)-(7x7) oxidation at 440°C. The dose was 3.4 L at $3 \times 10^{-9}$ torr. The topograph was measured at +0.6 V sample bias. The image size is $\sim 250 \, \text{Å} \times 250 \, \text{Å}$. Dark sites are believed to be the locations of reacted oxygen.
Figure 4.2 Si(111)-(7x7) oxidation at 540°C and 6x10^{-8} torr for a 6.0 L dose. (a) representative image for most of the surface. (b) shows a large monolayer deep hole which is not seen at lower oxidation temperatures. A faint pattern of adatoms can be seen at the bottom of the 3.1 Å deep hole. This provides evidence that at this oxidation pressure and temperature that surface etching does occur. Both images are ~460 Å x 460 Å.
Figure 4.3 Si(111)-(7x7) oxidation at 640°C and 5x10^-8 torr for a 10 L dose. (a) 520 Å x 520 Å area representative of most the surface. Note the low defect density. (b) 832 Å x 580 Å area near retracted surface steps that exposed new surface material which reconstructed to the 5x5, 7x7, and 9x9 structures. The steps retract due to the dominant oxidation-induced etching reaction.
Figure 4.4 Si(111)-(7x7) oxidation at 640°C, 3x10^{-7} torr, and a dose of 18 L. Area is approximately 700 Å x 500 Å. Again monolayer deep holes indicative of the etching process are evident. In this case the newly exposed surface at the bottom of the hole has reconstructed to the 5x5 structure as well as a unit cell of the 9x9 structure. Other dark sites may be true holes (3.1 Å deep) or reacted oxidized sites.
Figure 4.5 Top-view schematic of the mobile vacancy model. Vacancies are created by random SiO desorption from the terraces and step edges. Then the resulting vacancies diffuse around the surface, terminating at a step edge causing it to retract or coalescing with other vacancies to form a vacancy island.
Figure 4.6 Examples of newly exposed surface at the base of a retracted step edge. (a) newly exposed surface reconstructed to form the 5x5 structure, 540 Å x 370 Å. (b) newly exposed surface only partially reconstructed to the 7x7 while a large portion remained disordered. Image size is 540 Å x 400 Å. Both oxidations were done at 640°C.
Figure 4.7 Preferential B-type step retraction. (a) top-view greyscale STM topograph of 300x300 nm² area of clean Si(001)-(2x1) starting surface, miscut toward [110] to create distinct A- and B-type steps. (b) 28x28 nm² close-up showing typical starting defect densities. (c) 300x300 nm² area after 50 L O₂ at 2x10⁻⁸ torr and 640°C, showing reduction in area of B-type terraces. (d) ratio of A- to B-type terrace areas vs O₂ dose.
Figure 4.8 Pinning schematic. Once the pinning defect forms, the underlying material is prevented from etching. Prolonged etching under these conditions substantially roughens the surface.
Figure 4.9 Examples of pinning sites. Surfaces were all oxidized at 640°C and 6x10^-8 torr. (a) 30 L dose, 200x200 nm scan. The inset shows a strikingly linear defect which is pinning an island on finger complex. The white arrow indicates the early stage of the pinning mechanism. (b) 40 L dose, 246 Å x 154 Å scan. The white arrow indicates the pinning site after 1 ML has been removed locally. (c) 50 L dose, 200x200 nm scan. The white arrow shows a pinning site at close to 2 ML removal, and finally the circled island-on-island shows the pinning site after a complete 2 ML have been locally removed.
Figure 4.10 Si(001)-(2x1) oxidation at 640°C. (a) clean surface, (b) $2 \times 10^{-8}$ torr, (c) $4 \times 10^{-8}$ torr, (d) $6 \times 10^{-8}$ torr, (e) $8 \times 10^{-8}$ torr, and (f) $1 \times 10^{-7}$ torr. Higher pressures lead to more pinning sites which we believe are nucleated oxide clusters. All images are $-500 \times 500$ nm$^2$, and all have the same total exposure of 63 L.
Figure 4.11 Close-up (500 x 500 Å²) of the surface in Fig. 4.10(f). Under these oxidation conditions (640°C, 1x10⁻⁷ torr, 63 L) SiO₂ formation is occurring almost as rapidly as SiO is desorbing. The linear pinning defects have evolved into extended disordered regions of oxide patches. Ordered oxygen related sites (like those in Ref. 86) are marked with the arrows.
Figure 4.12 High-dose, oxide-capped cluster. Suggests the start of cone-shaped structures observed by Smith and Ghidini in Ref. 65. The bright apex area appears to be consistent with a disordered, oxidized patch capping silicon terraces which are distinguishable around the edges of this cluster. Scan size is $100 \times 100 \text{ nm}^2$. Oxidation conditions were $690^\circ \text{C}$, $1.5 \times 10^{-8}$ torr, and 410 L.
Figure 4.13 Si(001)-(2×1) oxidation sequence at 6×10⁻⁸ torr and 640°C. Data are shown as top-view greyscales and 3D perspectives to emphasize oxide cluster density saturation at high doses along with constant cluster height evolution. The constant cluster height evolution implies a constant vertical etch rate for the clean areas between the clusters. Note that the vertical axis is greatly expanded with respect to the lateral scale. (a) Dose is 100 L.
Figure 4.13 continued. (b) Dose is 200 L.
Figure 4.13 continued. (c) Dose is 400 L.
Figure 4.13 continued. (d) Dose is 800 L.
Figure 4.14 Sample area between oxide clusters showing evidence of remaining 2x1 surface reconstruction even after 800 L dose at 640°C and 6x10⁻⁸ torr. This indicates that the majority of the adsorbed oxygen is located in the clusters not between the clusters. Image size is about 400 Å x 400 Å.
Figure 4.15 Low dose pressure dependence. Cluster densities and corresponding nucleation rate. (a) Density of oxide clusters as a function of oxidation pressure. (b) Corresponding nucleation rate for the data plotted in (a). The power law dependence suggests that oxide nucleation is at least a second order process.
Figure 4.16 High dose pressure dependence. Oxide cluster densities are shown for series of oxidations all done at 690°C for (a) Si(001) and (b) Si(111). In each case three separate pressures were used as noted. Saturation cluster densities increase for higher pressures. Note that layers etched and dose are linearly dependent on oxidation time and 35 layers etched = 1100 L so the abscissas are the same. Solid lines are fits by rate equation analysis of the dual-species model discussed in Chapter 5. Dashed curves are Monte Carlo simulations using the same parameters as the rate equations.
Figure 4.17 Oxide cluster nucleation dependence on temperature. For these data a temperature gradient was established across a Si(001) sample. (a) The cool side of the sample shows a larger number of nucleated clusters than the warm side of the sample shown in (b). (c) Plot of the corresponding nucleation rate across the sample in an Arrhenius form to find an effective activation energy of -3.6 eV (solid line).
Figure 4.18 High dose, temperature dependence. Oxide cluster densities are shown for series of oxidations all done at 6x10^-8 torr for (a) Si(001) and (b) Si(111). In each case three separate temperatures were used as noted. Saturation cluster densities increase for lower temperatures. Rate equation analysis (solid lines) and Monte Carlo simulations (dashed lines) of the dual-species model (discussed in Chapter 5) show good qualitative agreement with the experimental data. These fits used the temperatures as read from the pyrometer. The dotted lines are rate equation solutions using the corrected actual temperatures.
Figure 4.19 Examples of different starting defect densities and the effect they have on subsequent nucleation kinetics. We believe that increased defect densities result in increased sticking for impinging oxygen molecules and therefore enhanced nucleation. The graph shows the measured decrease in cluster density with decreasing initial defect density. The dotted line is a guide to the eye.
Figure 4.20 Example of oxide cluster density dependence on sample miscut. (a) 690°C, 6x10⁻⁸ torr, 400 L oxidized Si(001) surface with ~0.1° miscut. About 18 clusters have nucleated. (b) same oxidation done on a Si(001) surface with a 3° miscut. About 64 clusters have nucleated. Both images are 500x500 nm².
Figure 4.21 Average cluster height evolution in time. (a) for Si(001). (b) for Si(111). Linear behavior implies a constant vertical etch rate on the clean areas between the oxide clusters. Relative etch rates are roughly consistent with the relative nominal pressures (as noted), etching faster at higher pressures. Inferred sticking coefficients from the amount of material removed are shown in Table 1.
CHAPTER 5

OXIDATION MODELS

5.1 The Single Species model

5.1.1 Support for the single species model

In Chapter 4 the experimental results of how oxide cluster nucleation depended on oxidation pressure, temperature, and dose conditions were presented. In this chapter we will propose various atomic-scale models in hopes of finding a single model consistent with all observed data. These models will be tested by rate equation simulation as well as Monte Carlo simulations to see if predicted cluster densities can be made to match with the observed densities by employing a single set of reasonable model parameters. As mentioned in Chapter 1, many of these fundamental parameters (e.g. the diffusion energy for oxygen on the surface of silicon) are essentially unknown. This means that considerable freedom may be used when selecting the appropriate parameters. Nevertheless, it will be shown below that even if a very wide range of parameters are used, some atomic-scale models will simply be unable to explain the experimentally observed data.
To begin, we will propose the following simple model shown schematically in Fig. 5.1: First we will assume that all oxygen molecules that react with the surface will dissociate quickly to form an oxygen “monomer” (a single oxygen atom possibly bonded to a single silicon atom). We make this assumption since it has been suggested from previous studies that molecular oxygen species are essentially absent above 300°C. Since we know that silicon monoxide desorption dominates under our oxidation conditions, it is reasonable to think of this oxygen monomer as a silicon monoxide molecule that has not broken the underlying Si=Si bond in order to desorb. It is important to note, however, that the specific bonding configuration of the oxygen atom is not important to the essence of the model nor critical to its results. For this simple model we will also assume that this monomer can diffuse around the surface, desorb causing etching, or find another diffusing monomer and nucleate an oxide complex (a bi-cluster with two oxygen atoms). In addition a diffusing monomer may also find an existing bi-cluster, attach to it, and cause it to grow.

Venables and coworkers have done extensive theoretical work on modeling similar nucleation and growth systems. In the course of examining example systems such as noble metals on alkali halides, a system of generalized rate equations was established. The basic physical properties represented in these equations are the same as we propose in the simple model above: adsorption, desorption, diffusion, nucleation and growth. However, it is important to recall that the corrosive nature of this particular system adds complexity to the traditional systems in that the substrate’s morphology changes both as a function of nucleation and growth, as well as from etching. In our case then, not only can a deposited atom desorb, but when it does so, an atom of the substrate goes with it. The possible
consequences of this added change in morphology from etching will be mentioned below.

The generalized equations determined by Venables are shown below:

\[ \frac{dn_i}{dt} = F - \frac{n_i}{\tau} - 2U_1 - \sum_{j=2}^{\infty} U_j \]  (5.1.1)

\[ \frac{dn_j}{dt} = U_{j-1} - U_j \quad (j \geq 2) \]  (5.1.2)

In these equations, \( n_i \) is the density of single adatoms (in our case oxygen “monomers”) on the surface and \( n_j \) is the density of islands (oxide clusters) of size \( j \) atoms. \( F \) is the reacted flux rate (which is the sticking coefficient, \( s_o \), times the impinging flux, \( \Phi \), which is just proportional to \( P_o \)) and \( \tau \) is the monomer’s lifetime before desorbing from the surface. The quantity \( U_i \) is the rate at which two monomers combine to nucleate a new cluster, and the quantity \( U_j \) is the rate for a cluster of size \( j \) atoms to capture one diffusing monomer (i.e. grow). All terms in these equations are rates with units: number per area per second. For numerical calculations in this work, units were normalized to a typical 5000 Å x 5000 Å scan area to facilitate comparison with experimental data.

Venables and coworkers went on to simplify these equations by classifying clusters as stable and unstable. Clusters of size \( j \leq i \) could decay by the detachment of a monomer, while clusters of size \( j > i \) were stable. Here \( i \) is defined as the critical size. With these definitions the Eqs. 5.1.1 and 5.1.2 become:

\[ \frac{dn_i}{dt} = F - \frac{n_i}{\tau} - \frac{d(n_s w_s)}{dt} \]  (5.1.3)

where \( n_s \) is the number of stable clusters with an average of \( w_s \) atoms per cluster,
\[ \frac{dn_j}{dt} = 0 \quad (2 \leq j \leq i) \tag{5.1.4} \]
due to a detailed balance argument for unstable clusters, and

\[ \frac{dn_i}{dt} = U_i \tag{5.1.5} \]

where

\[ U_i = \sigma_i D n_i n_i \equiv J \] (the nucleation rate of stable clusters) \tag{5.1.6}

Here, \( \sigma_i \) is a "capture number" for clusters of the critical size \( i \), and \( D \) is the adatom diffusion coefficient. The capture number may be thought of as a geometric factor which is proportional to the ability of a cluster to capture a diffusing monomer. In this manner it is similar to an effective cross-section, and should depend on the magnitude of the perimeter of a cluster or possibly the area of the cluster depending on the attachment mechanism for growth.

We will assume in this simple case, that only two monomers must come together to form a stable cluster, so \( i = 1 \). In other words, clusters of size two can grow, but can not break-up. The capture number \( \sigma_i \) then is the cross-section for one monomer to capture another. For single monomers this number is a constant value of order unity. As stated above these equations are based from simple systems in which chemical reactions involving substrate and adsorbate are not involved. In the silicon/oxygen system, however, chemical reactivity is very important. A stable oxide cluster that forms on the surface is not just oxygen, but SiO\(_x\). In this case it is reasonable to assume then that for a new stable oxide cluster to nucleate, substantial bonds must be broken and reformed to create a stable complex. This has the effect of introducing another activation energy into the problem.
which we will call the nucleation energy, $E_*$. A similar activation energy for attachment to an existing oxide cluster will also be employed, $E_g$ for growth. For simplicity it will be assumed that this growth energy will be the same for attachment of a monomer to any size of stable oxide cluster. With these considerations the rate equations above can be re-written:

$$\frac{dn_1}{dt} = F - \frac{n_1}{\tau} - 2\sigma_1 Dn_1^2 \exp\left(-\frac{E_*}{k_B T}\right) - \sigma_1 Dn_1 n_2 \exp\left(-\frac{E_g}{k_B T}\right)$$  \hspace{1cm} (5.1.7)

$$\frac{dn_2}{dt} = \sigma_1 Dn_1^2 \exp\left(-\frac{E_*}{k_B T}\right) = J_{\text{nuc}}$$ \hspace{1cm} (5.1.8)

As shown in the results of Chapter 4, all oxidation conditions presented here are in the limit of desorption dominated oxidation. Thus active oxidation dominates, and the resulting surface is always in a "low" oxygen coverage regime. Once the steady state of oxygen monomers has built-up on the surface, the left-hand-side of Eqn. 5.1.7 goes approximately to zero, and since the first two terms (adsorption and desorption) are much larger than the second two (nucleation and growth), we can see that $0 \approx F - n_1/\tau$. Thus in the desorption dominated regime, $n_1 \approx F\tau$. Substituting this relationship into Eqn. 5.1.8 means that $J_{\text{nuc}} \approx DF^2\tau^2 \exp(-E_*/k_B T)$. Recall that $F = 2s_0 \Phi$ where $\Phi$ is the impinging $O_2$ flux which is proportional to the oxidation pressure, and the factor of two comes from the fact that 2 oxygen atoms result from each reacted molecule. Therefore, from this simple model we see that $J_{\text{nuc}} \propto P_0^{-m}$ with $m=2$ in rough agreement with our measurements in which $m \approx 2.2-2.4$.

The fact that the measured pressure dependence is greater than a second power dependence suggests that bi-clusters (two monomers together) may in fact not be
completely stable by themselves. For example, it is possible that two monomers together are only partially stable, and that it really takes three monomers to form a stable cluster. If this is true, the rate equations must be modified to include the break-up of bi-clusters, and the critical size goes from \( i = 1 \) to \( i = 2 \). This case will be discussed below when attempting to reconcile the high dose dependence with the model’s behavior.

This simple model also predicts a temperature dependence. Temperature dependent quantities include the monomer lifetime (desorption limited), the diffusion coefficient \( D \), and explicitly the nucleation and growth Boltzmann factors. In the former cases the \( \tau = [1/\nu_a]\exp(E_a/k_bT) \) where \( \nu_a \) is the attempt frequency (or prefactor) for desorption and \( E_a \) is the activation energy for desorption. Typically, attempt frequencies are considered temperature insensitive and have values of typical phonon frequencies in the crystal (on the order of \( 10^{11}-10^{13} \) Hz). For the diffusion coefficient, \( D = (1/N_0)v_d\exp(-E_d/k_bT) \) where \( N_0 \) is the number of sites per unit area, \( v_d \) is the attempt frequency for diffusion, and \( E_d \) is the activation energy for diffusion. Taken together with Eqn. 5.1.8 and substituting \( n_i \approx F \tau \), we arrive at the final temperature dependence for the nucleation rate: \( J_{\text{ox}} \propto \exp[(2E_a - E_d - E_n)/k_bT] \) or \( J_{\text{ox}} \propto \exp[-E_{\text{eff}}/k_bT] \) where \( E_{\text{eff}} \) is the effective activation energy in an Arrhenius sense as introduced in Chapter 4.

From the data presented in Chapter 4, we recall that \( E_{\text{eff}} \) for the oxide cluster nucleation rate was between -3.3 and -4.0 eV. We may conclude then from this simple model that \( 2E_a - E_d - E_n = -E_{\text{eff}} = 3.3 \) to 4.0 eV. For the particular case of SiO desorption from the silicon surface, independent measurements by Memmert and Yu and Engstrom and coworkers have determined that \( E_a \approx 3.0 - 3.5 \) eV. Furthermore, we note that \( E_d \)
(oxygen surface diffusion) should be less than $E_d^{\text{bulk}}$ (oxygen bulk diffusion) which is approximately 2.4 eV.\textsuperscript{123} From these studies we cannot conclude specifics about either the diffusion or nucleation energy, but we can say that the sum of the two energies is likely between 2.0 and 3.7 implying that the nucleation energy is in fact a non-zero quantity. As can be seen then, this type of analysis is really most useful if many of the individual activation energies are known, since it is the sum $2E_n - E_d - E_n$ which determines the entire temperature dependence of the oxidation process in this simple model. Furthermore from this analysis it is clear why the net nucleation rate decreases when the temperature is raised: $2E_n > E_d + E_n$, thus resulting in a negative effective activation energy. To summarize then, this model is qualitatively consistent with the pressure- and temperature-dependent experimental observations at low doses and allows for reasonable values of the nucleation and diffusion energies.

We emphasize that this analysis is quite simple and that several important assumptions have been made. For example, it is possible that only clusters which have grown to a certain size will be able to pin steps, or that bi-cluster break-up cannot be neglected. These scenarios can be accounted for with the critical size, $i$. As suggested previously, surface defects could also play a role. In fact, we have found that highly defective surfaces do form fingers and clusters more quickly than clean surfaces. An example of this was shown in Fig. 4.19. This phenomenon may possibly be accounted for by dynamically adjusting the sticking coefficient, but efforts along these lines have not been made.
Further corroboration for this model has come from extensive Monte Carlo simulations performed by C. Ebner.\textsuperscript{93} It is important to realize that rate equation analysis is a mean-field approach to investigating kinetics, and thus may not be truly representative of the system under consideration. When used in conjunction with Monte Carlo (MC) simulations, however, they can be compelling support for a particular atomic-scale model. The MC simulations differ from the rate equations in that specific spatial information about surface morphology can be directly observed, since average rates for processes are replaced by specific probabilities for a given atomic process on a real lattice. In addition, surface relaxation was allowed and initial and final state energies were considered. In this most detailed form of the MC simulations, the surface was allowed to form or break the 2x1 reconstruction, form or remove antiphase boundaries, and both Si atoms and SiO molecules could diffuse around the surface. However, due to the large computation times (1 layer etched per day of computation), the model was simplified for extended dose simulations (>63 L), only allowing SiO to diffuse and essentially ignoring the 2x1 substrate. The MC simulations are described in detail in Ref. 93, and the primary conclusions are summarized below.

The first test was to see if the initial starting surface behaved properly under the well-known processes of epitaxial growth and ion sputtering. Consistent with the previous discussion of preferential growth and etching of B-type steps, the MC simulations showed in fact that B-type terraces grew faster than A-type during epitaxial growth and that B-type terraces were preferentially reduced in area during ion sputtering. In addition, the spatial information of the MC simulations could be used to show that depletion zones existed
around $S_\theta$ steps after growth, further suggesting that these steps provide a good sink for
diffusing adatoms. It should be noted that this type of spatial information is impossible to
extract from mean-field rate equations.

Under oxygen exposure the MC simulations of this simple model also reproduced
the experimentally observed surface morphology. Here, the MC simulations assumed that
if two "oxide monomers" nucleated a bi-cluster, that the underlying silicon and next-
nearest-neighbor dimers would be prevented from etching. Qualitatively the results from
these simulations showed that long silicon fingers could form around an oxide cluster and
that these fingers could be etched from the sides to leave an isolated oxide cluster. Also
observed in the simulations were silicon bridges (i.e. thin terraces) that extended between
oxide clusters which were also seen experimentally as in Fig. 4.9(c). Finally, from counting
the clusters formed in the MC simulations (which used the same activation energies and
precursors as the rate equations), good agreement was obtained with the experimental
pressure ($J_\alpha \sim P_{\alpha}^{-m}$ with $2 < m < 2.4$) and the temperature dependence ($J_\alpha \sim \exp(-\beta E_{\text{eff}})$ with
$-E_{\text{eff}} = 2E_a - E_a + E_a$) for the low dose experiments. From these results we found no substantial
difference between MC conclusions and rate equations implying that individual atomic
processes could be well approximated with average rates of reactions and spatial
correlations could be essentially neglected.

At the time this simple model was being considered with both rate equations and
MC simulations, we had not performed any extended dose experiments. With these new
experiments, however, we quickly realized that the simple single species model was
insufficient to explain the high dose data, as both the rate equation analysis and the MC
simulations were unable to reproduce the extended dose saturation with constant vertical etching that was observed experimentally.

5.1.2 Failure of the single species model

Recapitulating the simple model, we assumed that reacted oxygen dissociates on the surface to form diffusing “oxide monomers.” These could either etch the surface (via the desorption of SiO), join with another monomer to nucleate an oxide cluster, or attach to an existing cluster. Rate equation analysis and Monte Carlo simulations were used to examine the evolution of oxide clusters in time as a function of $P_\text{ar}$ and $T_r$. At low doses ($< 100$ L), predictions of this simple model were consistent with the measured pressure dependence and temperature dependence of the initial nucleation rate $J_{\text{ar}}$, assuming reasonable values for parameters controlling SiO desorption, monomer diffusion, and cluster nucleation.

However, we find that this model cannot account for the observed high-dose suppression of $J_{\text{ar}}$ together with the observed constant vertical etch rate. It is well known that cluster nucleation can in general be suppressed when a sufficient density of clusters is established to provide an efficient “sink” for diffusing monomers. This would reduce the monomer density on the surface, and hence suppress nucleation of new clusters. If, however, these same monomers are also responsible for SiO desorption, a reduction in the monomer density would suppress SiO desorption and hence suppress the vertical etch
A reduction in etch rate, however, is not observed experimentally. Therefore, this simple model as stated is insufficient to explain the oxidation behavior seen at high doses.

It is difficult to conceive what type of reasonable modification we can make to this model to achieve constant etching and the simultaneous suppression of oxide nucleation. One modification made was to incorporate bi-cluster break-up. Since some nucleation energy was required to form the bi-cluster in the first place, it is reasonable to assume that there is another activation barrier to be overcome when a bi-cluster breaks-up; we call this energy $E_b$. With this addition, we must now track the population of bi-clusters during a rate equation or Monte Carlo simulation. Now oxygen monomers can be lost to desorption, the nucleation of a bi-cluster, the growth of a bi-cluster (i.e., the nucleation of a stable cluster), or the growth of a stable cluster. Furthermore, in addition to the reactive flux, we may also gain two oxygen monomers from bi-cluster break-up.

With these modifications, Eqns. 5.1.7-5.1.8 become:

$$\frac{dn_1}{dt} = F - \frac{n_1}{\tau} - 2\sigma_1 Dn_1^2 \exp\left(-\frac{E_n}{k_bT}\right) - \sigma_2 Dn_1 n_2 \exp\left(-\frac{E_g}{k_bT}\right) - \sigma_2 Dn_1 n_2 \exp\left(-\frac{E_g}{k_bT}\right) + 2n_2 \exp\left(-\frac{E_g}{k_bT}\right)$$

(5.1.9)

$$\frac{dn_2}{dt} = \sigma_1 Dn_1^2 \exp\left(-\frac{E_n}{k_bT}\right) - \sigma_2 Dn_1 n_2 \exp\left(-\frac{E_g}{k_bT}\right) - n_2 \exp\left(-\frac{E_g}{k_bT}\right)$$

(5.1.10)

$$\frac{dn_2}{dt} = \sigma_2 Dn_1 n_2 \exp\left(-\frac{E_g}{k_bT}\right) = J_{ax} \quad \text{(the nucleation rate)}$$

(5.1.11)

The above rate equations were solved numerically with fourth order Runge-Kutta in order to see if cluster nucleation could be suppressed while etching remained constant. The results were negative. Although bi-cluster break-up could be used to enhance the
power law dependence of cluster density on oxidation pressure to be more consistent with the observed exponent of $m = 2.4$ (i.e. $J_\alpha \propto P_\alpha^m$; with $2<m<3$), this break-up term did not do anything to separate the interdependence of the nucleation rate and etch rate. As a result, suppressed oxide cluster nucleation could only be achieved at the expense of etch rate suppression. These results were confirmed with both rate equation calculations and MC simulations.93

Another modification that was tried involved incorporating oxide cluster coalescence into the model. If oxide clusters were growing together this would reduce the number density or at least cause a decrease in the effective nucleation rate. Such a decrease would manifest itself as a roll-over (or saturation) in the oxide cluster density as a function of time or dose. A few very large dose experiments were conducted, however, and even at 2000 L, no evidence of a decrease in cluster density was observed, only a saturation in cluster density. With a coalescence term in the model, MC simulations found that a prolonged saturation regime did not exist, but rather as soon as the cluster density saturated, it very quickly thereafter began to decrease.93 Again, this is in contrast to our extended dose experimental observations and is inconsistent with the general appearance of STM images which show that even when clusters are very close together, the individual apex of each cluster may be distinguished and hence counted separately.

Finally, there may be other considerations which we have not taken into consideration. One of these considerations which has not been incorporated into the model is strain. It is possible that with simultaneous nucleation and etching that sufficient strain builds up, possibly around clusters, so that the diffusion and/or
nucleation rates are altered. It is difficult, however, to envision how this type of strain would suppress the nucleation of new islands at high doses.

Another possibility is that the etching process can create new step edges which may alter the sticking coefficient as we have seen above with the high miscut silicon. Again, however, it is difficult to see how the creation of new step edges could suppress subsequent nucleation. In fact, we would expect from the arguments in section 4.5.2 that an increase in step density would increase the sticking coefficient which is similar to raising the pressure, and hence an increase in nucleation might be expected. This is certainly not observed at high doses, where it is clear that growth (not nucleation) is dominating. Furthermore, if oxygen was sticking only at step edges that might explain why nucleation is suppressed (since all the newly reacted oxygen would essentially be part of an oxide cluster to begin with, i.e. growth by "direct" impingement), but this would not explain the constant vertical etching on clean terraces between the oxide clusters.

Another consequence of an increased local step density (especially around clusters) may be an altered diffusion rate. If, for example, one assumes it is harder for oxygen to diffuse up a series of steps, then this would imply that the density of oxygen monomers on the flat areas between clusters should be increased. This, however, would lead to increased nucleation which is not observed. If it is easier to diffuse up step edges, this may suppress subsequent nucleation by making existing clusters more effective sinks for diffusing oxygen species, but as stated previously this would not be consistent with
the observed constant etch rate which should also decrease with a decreasing density of oxygen monomers.

Satisfied that this simple model was not going to be able to reproduce our experimental observations regardless of parameters used or simple modifications made, we decided to shift our attention to alternate models. Again the main focus of our search would be to develop a model which lessened the interdependence of the oxide nucleation rate and etch rate.

5.2 The Dual-Species Model

5.2.1 Description

We next considered an alternate model which lessened the interdependence of $J_\alpha$ and $\eta$ by assuming that two different oxide-monomer species are responsible for SiO desorption and oxide cluster nucleation, respectively. In fact such a model had already been proposed by Engstrom et al.\textsuperscript{73} based entirely on macroscopic measurements of oxide growth and SiO desorption. This model (shown schematically in Fig. 5.2) assumes that reacted oxygen atoms first form a “desorption precursor” (top-center Fig. 5.2), which can either desorb from the surface as SiO (at rate $k_{\text{des}}$), or convert (at rate $k_{\text{con}}$) to possibly a bridge- or back-bonded configuration (bottom-center Fig. 5.2). This back-bonded species could also convert back to a precursor (at rate $k^*_{\text{con}}$). As in the simple single species model, the exact bonding configurations for these species are unknown, and the
depictions of each in Fig. 5.2 are only possibilities. Again it must be emphasized that the quantitative predictions of the model are completely independent of the particular bonding configurations. Both species can then diffuse across the surface (at rate $k_{df}$), but only the back-bonded species can lead to oxide cluster nucleation (at rate $k_{nc}$) or growth (at rate $k_{gr}$) while only the desorption precursor can cause etching. Clusters of two were allowed to break-up (at rate $k_{break}$), while clusters of three or more were assumed stable.

A necessary requirement for this type of model to account for the observed behavior is that $k_{df} \gg k_{cf}$. In this case $\eta$ remains roughly constant since most reacted oxygen atoms simply desorb as SiO before they convert to the back-bonded form. However, the population of the (minority) back-bonded species that does form shows large variations with time, and becomes depleted when a sufficient oxide cluster density develops. Hence, cluster nucleation is suppressed at higher doses without significantly affecting $\eta$.

With this new model the rate equations now have the following form:

$$\frac{dn_p}{dt} = F - \frac{n_p}{\tau} - k_{con}n_p + k_{con}^*n_b$$  \hspace{1cm} (5.2.1)

$$\frac{dn_b}{dt} = k_{con}n_p - k_{con}^*n_b - 2\sigma_1 Dn_b^2 \exp(-E_a/k_bT) - \sigma_2 Dn_2 n_2 \exp(-E_a/k_bT) - \sigma_z Dn_b n_z \exp(-E_g/k_bT) - n_2 \exp(-E_z/k_bT) + 2n_z \exp(-E_z/k_bT)$$  \hspace{1cm} (5.2.2)

$$\frac{dn_2}{dt} = \sigma_1 Dn_2 \exp(-E_a/k_bT) - \sigma_2 Dn_3 n_2 \exp(-E_g/k_bT) - n_2 \exp(-E_z/k_bT)$$  \hspace{1cm} (5.2.3)

$$\frac{dn_z}{dt} = \sigma_2 Dn_b n_2 \exp(-E_g/k_bT) \equiv J_{nx}$$  \hspace{1cm} (the nucleation rate)  \hspace{1cm} (5.2.4)
These equations were solved numerically with fourth order Runge-Kutta and a qualitative consistency could be obtained with the measured data using a single set of reasonable parameters. The specific C code to solve these equations appears in the appendix, and the results are indicated by the solid lines in Fig. 4.16 and Fig. 4.18 and the dashed line in Fig. 4.17.

One important note here is that at the time these simulations (both rate equations and MC) were run, the temperatures being used were the temperatures as read from the pyrometer which we now believe to be underestimates of the actual temperature by about 40°C (see discussion in Chapter 2). Of course the relative temperatures are still the same, and since the absolute shift is relatively small, most of the difference in predicted cluster densities can be compensated for by small changes in the energies. Thus individual activation energies used for either set of temperatures (i.e. pyrometer values or actual) should not differ by more than 0.1 eV. So again, the simulation results (solid and dashed lines) shown in Chapter 4 are based on the pyrometer temperatures not the actual temperatures reported in Figs. 4.16 and 4.18. Furthermore, all reported simulation results of this chapter will be based on the original pyrometer temperatures as well.

As a check, however, rate equation simulations we run again with small (<0.1 eV) adjustments to the conversion energies between the two species of the dual-species model. The results from these simulations are shown by the dotted line in Fig. 4.18. It should be emphasized that very little effort was made to reproduce the exact fits obtained at the pyrometer temperatures. Nevertheless, reasonable agreement between the model’s predictions and the experimental data (especially for the saturation level) is maintained.
In this case all activation energies and prefactors are the same as those used for the pyrometer temperatures except for the values of $E_{\text{con}}$ and $E_{\text{con}}^*$ as noted below. Certainly with more effort these fits could be improved, possibly by changing different energies.

Therefore, even with this temperature discrepancy, the model's predictions do show the correct temperature and pressure dependencies for the saturation cluster density, and the saturation onset at ~5 layers etched. Monte Carlo simulations (dashed lines in Fig. 4.16 and 4.18) with similar parameter values to those previously discussed also show the correct qualitative behavior. Simulations of this dual species model are also reasonably consistent with the initial nucleation rate $J_{\text{in}}$ measured for doses $\leq 150$ L. These simulations also do result in a nearly constant vertical etch rate $\eta$ over the duration of the simulations as shown below in section 5.2.2.

### 5.2.2 Species population tracking

To fully understand how this model achieves cluster density saturation with simultaneous constant vertical etching, it is useful to graphically track the populations of the species involved during the course of a simulation. Figures 5.3(a) and (b) show the nucleation and etch rates for Si(001) and Si(111) respectively as a function of time (calculated by the rate equations). As indicated above, these rate equations result in the correct behavior for both a falling nucleation rate and a constant vertical etch rate at high doses. Since the etch rate is directly proportional to the number density of precursor species, it is reasonable that the density of precursor species has the same time profile as
the etch rate (Fig. 5.4). Furthermore the density of back-bonded species and two clusters should show the same general behavior as the nucleation rate, and this is also confirmed in Fig. 5.4. It should be noted that the nucleation of new islands is suppressed because the number of bi-clusters goes approximately to zero at long times. The reason for this can be traced back to the growth term (fourth term) of equation 5.2.2. As the size and number of oxide clusters grows on the surface, the effective capture cross-section (as defined in Eq. 5.1.6) increases to the point where the growth term is larger than the others which detract from the back-bonded density. This can be seen in the appendix where the magnitudes of the various terms are plotted as a function of time for various oxidation conditions. The increasing capture number is shown in Fig 5.5(a).

Another quantity of interest is the total number of oxygen atoms condensed into stable islands on the surface. This is tracked so that the capture number can accurately approximate the perimeter of an average oxide cluster. Once the saturation regime is reached, it can be seen that the total oxygen coverage increases linearly (at a slow rate) for the rest of the oxidation. Total oxygen coverage is depicted in Fig. 5.5(b) and reaches a maximum of about 6% for the Si(001) simulations. This value is consistent with the approximations presented in Chapter 4.

5.2.3 Parameter discussion

Since most reacted oxygen atoms desorb as SiO, the reacted-oxygen flux rate \( R_o \) (equal to the incident oxygen flux times a sticking coefficient of about 4%) could be
directly determined from the measured etch rate for each curve (see Table 1). The desorption activation energy \( (E_a = 3.3 \text{ eV}) \) and prefactor \( (4 \times 10^{18} \text{ s}^{-1}) \) for \( k_{\text{des}} \) were taken from Ref. 73. The other activation energies in the rate equation analysis were \( E_{\text{con}} = E^*_{\text{con}} = 2.8 \text{ eV}, E_d + E_a = 2.6 \text{ eV}, E_d + E_g = 2.2 \text{ eV}, \) and \( E_b = 2.25 \text{ eV}. \) For simplicity all prefactors (except for \( k_{\text{des}} \)) were set equal to \( 5.0 \times 10^{12} \text{ s}^{-1}. \) Note that the rate for cluster nucleation is assumed equal to the product of a monomer diffusion term times a reaction probability \( P_{\text{nuc}} = \exp(-E_d/k_B T) \) (with analogous terms for cluster growth), so that only the sum energies \( E_d + E_a \) and \( E_d + E_g \) appear in the rate equations. Here, \( E_a \) and \( E_g \) would presumably correspond to a bond-breaking energy required to form a cluster. The capture number for a stable cluster was proportional to the cluster perimeter. We should also note that the “precursor” species may diffuse as well, but since it does not directly lead to nucleation or growth, its diffusion rate has no bearing on the model predictions.

As mentioned above, these activation energies were determined from simulations based on pyrometer temperature readings rather than the actual temperatures. Increasing these temperatures by 40°C to the actual temperatures was compensated for in the activation energies by changing the relative values of \( E_{\text{con}} \) and \( E^*_{\text{con}}. \) For the original simulations both values were set to 2.78 eV. For simulations with the corrected temperatures, these values were changed to \( E_{\text{con}} = 2.70 \text{ eV} \) and \( E^*_{\text{con}} = 2.85 \text{ eV}. \) The results with these corrected energies are shown by the dotted lines in Fig. 4.18. Since the actual temperatures were higher, it was necessary to get more desorption precursors converted to back-bonded species. One way to easily accomplish this was to change these conversion energies. Certainly there are other possible ways to achieve this goal,
some probably better at reproducing the initial onset of saturation, but efforts along these lines were not explored. Furthermore, it must be emphasized that there is considerable freedom in moving both the activation energies and prefactors over a wide range of values. The point here is that with a single set of reasonable energies and prefactors, the dual-species model can reproduce the observed experimental behavior (regardless of which temperatures were used).

Admittedly, this model contains a number of adjustable parameters which are not known accurately from independent measurements. However, the values do appear reasonable. We expect that the surface oxygen diffusion energy $E_d$ should be less than the bulk diffusion energy of 2.4 eV, so the energy sums $E_d + E_n = 2.6$ eV and $E_d + E_g = 2.2$ eV can easily be satisfied with moderate, non-zero values for $E_n$ and $E_g$. In fact, these values are roughly consistent with reported energy values for surface oxygen diffusion $E_d = 1.0$ eV, and oxide nucleation $E_n = 1.5$ eV. The main point here is that this dual species model with a single set of reasonable parameter values shows very good qualitative consistency, with the pressure and temperature dependencies of initial oxide cluster nucleation, growth, and saturation. This lends the first strong microscopic support for a dual species oxidation model such as that proposed by Engstrom, et al. The STM measurements can give direct information about typical diffusion lengths for surface oxygen. In order for existing clusters to suppress nucleation of new clusters, the surface diffusion length $L_{df}$ must be at least as long as the typical cluster spacing $L_{cha}$. For example, we see from Fig. 4.18 that at saturation $L_{cha} > 100$ nm at 690°C and $P_{at} = 6 \times 10^4$ torr, which sets a lower limit of $\sim 100$ nm for the $L_{df}$
under these conditions. This limit is well within the simulated diffusion lengths with the parameter values assumed above.

5.3 Analytic Scaling Analysis

Much attention has recently been focused on the idea that nucleated island number densities and sizes can exhibit scaling behavior as some functional form of substrate temperature and source flux. This type of scaling analysis has a general appeal because it suggests the possibility of achieving the same surface morphology for different combinations of flux and temperature. Technologically, this flexibility in choosing different growth conditions to achieve a given surface morphology is very valuable since many modern materials impose strong restrictions on the range of viable growth conditions. The focus of this section will be to review how scaling evolves from nucleation models and apply this analysis to oxide cluster nucleation on silicon surfaces.

5.3.1 Scaling Theory

In general, scaling refers simply to any quantity that shows the same functional form when multiplied by the appropriate factor. Systems that exhibit scaling are systems that have scale invariance or self-affine structures. These are systems that have the same form (either actual or statistical shape) regardless of the length scale (or magnification) at which they are observed. With the recent popularity of fractal analysis, this term has
become a "key word" in the literature, and many researchers are looking for scaling behavior in their systems. This section will examine a variation of scaling which looks not at shape or structure, but rather at the number density of nucleated islands as the scaling quantity. In this case, the number density of islands resulting from different growth conditions can be scaled to the same value by multiplying by \((f(D,\tau_{des},F,Z))^\chi\) where \(D\) is the diffusion rate, \(\tau_{des}\) is the desorption rate, \(F\) is the flux rate, \(Z\) is the coverage, \(\chi\) is the scaling exponent, and \(f\) is some functional form which is very much dependent on the model used to explain the nucleation.

As suggested above, the first step in determining a scaling relationship is to postulate a working model for how the surface evolves during growth. In general, a model is assumed in which atoms are deposited at random on a clean, vicinal surface. These 'adatoms' may then (i) desorb from the surface, (ii) diffuse around the surface until they find another diffusing adatom and nucleate a new island, or (iii) attach to an existing island and cause it to grow. Desorption, nucleation and growth are common to most all models for surface evolution, so this basic model will be the starting point for examining scaling behavior. To extract the scaling form from such a model, it is convenient to write down the mean field rate equations for the populations of interest. This has been quite thoroughly addressed by Venables\(^{11,12}\) and has been introduced in section 5.1. The basic equations with which to begin are Eqns. 5.1.3 - 5.1.6 which are re-written below for reference:

\[
\frac{dn_t}{dt} = \frac{n_t}{\tau} - \frac{d(n_t w_t)}{dt} \quad (5.3.1)
\]
where \( n_j \) is the number of stable clusters with an average of \( w_j \) atoms per cluster,

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

(5.3.2)

due to a detailed balance argument for unstable clusters, and

\[
\frac{dn_i}{dt} = U_i
\]  

(5.3.3)

where

\[
U_i = \sigma_i D n_i n_i = J \text{ (the nucleation rate)}
\]  

(5.3.4)

Here, \( \sigma_i \) is a “capture number” for islands of the critical size, and \( D \) is the adatom diffusion coefficient.

The task now is to obtain an analytic solution to Eqs. (5.3.1)-(5.3.4). This problem has been discussed in the literature since the mid-1960s, and the solution is by no means trivial. In fact, in order to obtain any solution analytically, many assumptions need to be made. Stowell and Hutchinson\textsuperscript{124} first suggested that various regimes of growth needed to be examined separately (e.g. high temperature or low temperature; incomplete condensation, initially incomplete condensation, or complete condensation). Also, the form of the equations changes depending on whether 3D or 2D islands are being examined. The dimension of the islands primarily affects the capture cross-section of a given island and changes quantities like the total number of condensed atoms at coalescence. Although oxidation is known to extend into the bulk, HF dipping of our oxidized surfaces suggests that the oxide clusters are at most “capped” with a thin layer of oxide. These experiments (done in air) showed basically the same cluster heights and densities before and after the HF dip which strips all oxide on the surface. This being the

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case, only the case of 2D islands will be addressed here. Rather than solving these
equations for all the conditions mentioned above, the assumptions for each will be
summarized and the resulting form for the number of stable islands noted.

First, the high temperature case is considered. Here, adsorption and desorption
reach an equilibrium so as to make $dn_i/dt \to 0$. In this case, the loss of adatoms to
nucleation and growth may be assumed to be much smaller than the loss to desorption,
and thus by inspection of Eq. (5.2.1) we see $n_i \approx F \tau$. Finally, an expression for the
density of unstable clusters is needed. This problem has been solved by Walton, and his
result for the normalized density of unstable clusters is as follows:

$$\left( \frac{n_j}{N_0} \right) = \left( \frac{n_i}{N_0} \right)^j \sum_m C_j(m) \exp[\beta E_j(m)] \quad (2 \leq j \leq i)$$

(5.3.5)

In this relation, $N_0$ is the normalizing number of lattice sites, $\beta$ is $1/k_B T$ (with $k_B$
Boltzmann’s constant), and $C_j(m)$ is a statistical weight for the occurrence of the $m$th
configuration of an island with $j$ total atoms. $E_j(m)$ is similarly the binding energy of the
$m$th configuration of $j$ atoms. Substituting this relation with $j = i$ and the value for $n_i (= F \tau)$ into Eq. (5.2.4) indicates that the nucleation rate $J$ is then

$$J = \sigma_i D (F \tau)^{i+1} C/N_0^{-i} \exp[\beta E_i].$$

(5.3.6)

Under these high temperature conditions, a scaling relation between the
nucleation rate and the flux is clearly evident, $J \sim F^{i+1}$. By measuring $J$ as a function of
$F$, the critical cluster size can then be extracted. Once $i$ is known, the temperature
dependence of $J$ may be used to extract information about the activation energies for
diffusion ($E_d$), desorption ($E_a$), and nucleation ($E_n$) or binding ($E_b$). The temperature

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dependence of Eq. (5.3.6) is just: $J \sim \exp\{\beta[(i+1) E_s - E_d + E_i]\}$ which is clear with $D = \frac{1}{4} \nu N_0 \exp(-\beta E_d)$ and $\tau = \nu \exp(\beta E_d)$, with $\nu$ being an attempt frequency of $\sim10^{12}$ Hz.

The reader may recall that this is a similar result to that obtained by the simple model in section 5.1.1. For the simple model, however, the binding energy was not considered and was replaced by a positive nucleation barrier so that $E_i \to -E_n$. Also it should be noted that both results are contingent upon being in a high temperature, desorption-limited regime.

At lower temperatures the concentration $n_i$ is limited by nucleation and growth. For this case a form for $d(n_i \sigma)/dt$ must be determined. Venables and co-workers have examined this regime and have found:

$$\frac{d(n_i \sigma)}{dt} = (i + 1) U_i + \sigma D n_i + FZ$$

(5.3.7)

where the right hand side terms are nucleation, growth, and growth by direct impingement respectively. Here $Z$ is the fraction of the total surface that is covered with islands, and its rate of change is related simply to $n_s$'s by

$$\frac{dZ}{dt} = \Omega \frac{d(n_i \sigma)}{dt}$$

(5.3.8)

where $\Omega$ is the atomic volume of the flux.\textsuperscript{11}

With Eqs. (5.3.1-5) and Eqs. (5.3.7) and (5.3.8), it is possible to solve analytically for the scaling relations for $n_s$ (the stable cluster density) by using $Z$ as the independent variable and making assumptions about the growth regime. Many authors have contributed to solving this system of equations in various growth
and the results have been summarized by Venables et al. as follows:

$$\left( \frac{n_z}{N_0} \right) \sim Z^{(i+2)} \left( \frac{F}{N_0 \nu} \right)^x \exp(\beta E) \quad (5.3.9)$$

with the regime specific information summarized below in Table 2.

**Table 2.** Scaling exponents and generalized energy for various condensation regimes.

<table>
<thead>
<tr>
<th>Condensation Regime</th>
<th>Condition</th>
<th>$E$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extreme Incomplete</td>
<td>$\sigma_z D \tau n_z &lt;&lt; Z$</td>
<td>$E_i + (i+1)E_d - E_d$</td>
<td>1</td>
</tr>
<tr>
<td>Initially Incomplete</td>
<td>$Z &lt; \sigma_z D \tau n_z &lt; 1$</td>
<td>$\frac{1}{2} (E_i + i E_d)$</td>
<td>$i/2$</td>
</tr>
<tr>
<td>Complete</td>
<td>$\sigma_z D \tau n_z &gt;&gt; 1$</td>
<td>$(E_i + i E_d) / (i+2)$</td>
<td>$i / (i+2)$</td>
</tr>
</tbody>
</table>

With these results, we may now try to map our more complex model into that of the simple model so as to use the results shown above.

### 5.3.2 Scaling consequences for the dual-species model

Although the dual-species model is considerably more complex than the simple model proposed in Section 5.1.1, it can be examined with scaling analysis in certain limiting regimes. To determine the relevant regime one must look at the quantity $\sigma_z D \tau n_z$ and determine what the corresponding term would be for the dual-species model and in
doing so essentially map the behavior of the dual-species model into that of a simple model with the solutions shown above.

To find a simple analytic relation, we must go back and consider the corresponding nucleation model in Fig. 5.2. Recall that to maintain the constant vertical etch rate, the population of desorption precursors at all times is essentially constant. This means that the rate of conversion of precursors to back-bonded species is approximately constant in time as well. This conversion rate can now be considered the "incident flux" of nucleating (or growing) species. From this fact alone we can see the added complexity, since now the "flux" of nucleating species is itself temperature dependent in such a way as to include the precursor's desorption energy \( E_d \) as well as the conversion energy between precursor and back-bonded species \( E_{con} \). With this modification we can see that with respect to the back-bonded oxygen species, we again have the simple model where now the flux is temperature dependent (but approximately constant through the course of an oxidation), and the desorption energy is just the conversion energy to go from the back-bonded to the desorption precursor. We should also note that the nucleation energy is absent from the work of Venables et al., but it can be readily included in either the capture number or the diffusion factor for our more complex chemically reactive system. Thus \( D \) in the scaling results should be replaced with

\[
D' = 4vN_0^{-1}\exp(-\beta E_d)\exp(-\beta E_a).
\]

With these substitutions the quantity \( \sigma_\nu D\tau n_x \) now becomes \( \sigma_\nu D' \tau_{con}^\star \).

Values for this quantity during the oxidation conditions of Fig. 4.16 and 4.18 are shown in Fig. 5.6. As can be seen from the graphs the growth regime is usually in what

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Venables labels the initially incomplete condensation regime. These condensation regimes refer to the conditions experienced by the nucleating species. Physically, this regime means that the desorption term (or in our case, the back conversion term to the desorption precursor) and the growth term are of comparable magnitude (see Fig. A.2 in the appendix). For the extreme incomplete regime, almost all of the nucleating species are desorbing (or again, in our case, converting back to the desorption precursor), thus leaving the surface in an extremely low coverage limit. For the complete condensation regime, almost all the nucleating species find other diffusing species and nucleate or find existing islands and cause growth and subsequently coalescence. Clearly from the simulations, and consistent with the observed data, we are mostly within the intermediate regime of initially incomplete condensation. Again it is important to realize that although desorption is the dominant process seen experimentally (suggesting an incomplete condensation regime for the overall model), with respect to the nucleating species, the system is actually in an initially incomplete condensation regime. Venables points out that in this regime, although condensation is incomplete, clusters capture adatoms by surface diffusion, so that the growth term (5th term) is the largest in Eqn. 5.2.2.

This fact can be seen by observing the relative magnitudes of the desorption (i.e. conversion to precursor) term and the growth term (shown in the appendix, Fig A.2). Overall then, a desorption precursor is much more likely to desorb than to convert to a back-bonded species, but a back-bonded species is just slightly more likely to attach to an island and grow than it is to convert back to a desorption precursor. This being the case the scaling relation that is appropriate for this model is simply the scaling relation shown
in Eq. (5.3.9) with the regime taken to be initially incomplete condensation. The only difference is that now $F'$ (the flux of nucleating species) has temperature dependence. Since the concentration of precursors goes as $n \sim F\tau$, the "incident flux" of nucleating species, $F'$, goes as $F' \sim F\tau \cdot \exp[-E_{\text{con}}/k_B T]$. Recalling that $\tau \sim \exp(+E_a/k_B T)$ gives the final temperature dependence for $F' \sim F\exp[(E_a - E_{\text{con}})/k_B T]$. Thus in Eq. (5.3.9), $F$ should be replaced with $F'$ yielding:

$$\left(\frac{n_s}{N_0}\right) \sim Z^{1/2} \left(\frac{F}{N_0^{1/4}}\right)^x \exp\{\beta \chi (E_a - E_{\text{con}})\} \exp(\beta E)$$

(5.3.10)

where $E$ is the generalized energy given in Table 2 for the initially incomplete condensation regime with the one important change noted above. The desorption energy is now replaced by the back-bonded to desorption precursor conversion energy, $E^*_{\text{con}}$, since the back-bonded species is in essence "desorbing" into a precursor species. Finally, with these substitutions, the predicted scaling form for the number of stable islands is

$$\left(\frac{n_s}{N_0}\right) \sim Z^{1/2} \left(\frac{F}{N_0^{1/4}}\right)^x \exp\{\beta \chi (E_a - E_{\text{con}}) + \frac{1}{2} (E_i + iE^*_{\text{con}})\} \text{ with } \chi = i/2.$$

(5.3.11)

Now we can go back to the experimental data and look in the initially incomplete condensation regime for the cluster density as a function of $P_{\text{ar}}$ in order to get $\chi$. From Fig. 5.6 we see, however, that we are only completely within this regime at low doses for all the various Si(001) oxidation conditions (640-690°C, 3-12x10^4 torr). This being the case, we can appeal to the low dose pressure dependent data shown in Fig. 4.15. These data are re-plotted on a log-log plot of $n_s$ vs pressure in Fig. 5.7 where it can be seen that the slope, $\chi$, is 1.4 which implies that $i = 2.8$. We should note that this is more consistent
with what we would expect from the dual-species model where a 2-cluster can break-up
but a cluster of 3 oxygen atoms is stable. In fact, this result suggests that we may even
have to allow 3-clusters to break-up and start with clusters of 4 atoms being stable.

In any case, with the critical size now known, we can plot the number of stable
islands as a function of 1/T to examine the temperature dependence. Again, since we are
in the low dose regime, we can see the temperature dependence plotted for us already in
Fig. 4.17. Recall that under these conditions we found an energy dependence of 3.3 to
4.0 eV. The predicted slope from Eq (5.3.11) is then \([E_a - E_{com} + \frac{1}{2} E_i + 1.4 E^*_{com}] / k_B\].
Unfortunately then, under our initially incomplete conditions, we cannot determine any
restrictions on the diffusion, nucleation, or growth energies. Nevertheless, with
reasonable values of \(E_a\), \(E_{com}\), \(E^*_{com}\) and \(E_i\), this relation can be satisfied. In fact using the
same parameters used to fit the data in Fig. 4.16 and Fig. 4.18, and substituting \(E_i \rightarrow -E_a\)
\((3.33 - 2.78 - \frac{1}{2} 1.6 + 1.4 \times 2.78 = 3.64\ eV)\), we find that the scaling analysis is consistent
with the experimental data, and it is therefore also consistent with the numerical solution
of the rate equations (as it should be provided that mapping of the dual species model
back into a simple model was done correctly).

Due to the lack of independently determined values for these quantities, however,
further pursuit of this scaling analysis may be futile. One way to help this analysis would
be to perform experiments which were chosen in such a way as to place the system within
an extreme incomplete condensation regime or a complete condensation regime. This
way two more equations could be used to restrict the possible values for the parameters.
Even then, independent measurement of some of these values will probably be needed to gain any additional quantitative information on the kinetics of silicon oxidation.

5.3.3 Experimental scaling

Although the analytic scaling relationship is somewhat inconclusive as to the determination of specific activation energies, we can say that the oxygen/silicon system nevertheless does exhibit qualitative scaling behavior. Figure 5.8 shows an example of how the overall appearance of the surface morphology can be made to look the same if the pressure and temperature are both changed appropriately. In this case, an oxidation at 640°C and 2\times10^{-8} \text{ torr} results in an essentially identical surface as an oxidation done at 740°C and 1\times10^{-6} \text{ torr}. For reference it should be recalled that even a 1\times10^{-7} \text{ torr} oxidation at 640°C looks substantially different (Fig. 4.10(f) and Fig. 4.11) as an oxide film begins to form. These results suggest that it may be possible to get very similar surface morphologies (with respect to silicon etched and oxide nucleated) over a large range of temperatures simply by adjusting the oxidation pressure accordingly.

Scaling theory has been reviewed as a means for extracting kinetic information from atomic-scale nucleation models. For a minimal nucleation model, the general scaling relation was found to be Eq. 5.3.11 with the scaling exponent, \( \chi \), dependent on the growth regime as indicated in Table 2. The complex \( \text{O}_2/\text{Si} \) system was investigated. Here it was found that the minimal nucleation model was not sufficient to account for island density saturation and a constant vertical etch rate. As a result, a two species
model was adopted to explain the observed data. The scaling behavior of this two species model was then successfully mapped back to the minimal model with the appropriate substitutions to achieve potential consistency with the observed STM data, but without further independent determination of additional activation energies, quantitative conclusions are impossible. Qualitatively scaling was shown by surface morphologies resulting from oxidation at 640°C and 740°C under different oxidation pressures.
Figure 5.1 The Single-Species Oxidation Model. In this model the same oxygen configuration is responsible for nucleation, growth, and etching. The oxygen’s specific bonding configuration is not important to the essence of the model.
Figure 5.2 The Dual-Species Oxidation Model. In this model one species is responsible for etching and another oxygen configuration is responsible for nucleation and growth. This separation provides for the suppression of oxide cluster nucleation at high doses concurrent with constant vertical etching. Again the bonding configurations are only possibilities and the specific configurations are unimportant to the model.
Figure 5.3 Etch and Nucleation rates as generated by rate equation analysis of the dual-species model. Temperatures are based on the pyrometer readings and underestimate the actual temperature by ~ 40°C. The actual oxidation flux was chosen to yield the appropriate measured etch rate. Different oxidation conditions are noted in the legend which is the same for all four graphs. Etch rates are approximately constant throughout the oxidation while the nucleation rate is suppressed strongly at high doses. (a) rates for Si(001).
Figure 5.3 continued. (b) for Si(111). Again, the legend is common for all graphs, including Figs. 5.4 and 5.5.
Figure 5.4 Population profiles for desorption precursors (top linear curve in each) and back-bonded species (non-linearly decreasing curves). Dash of curve indicates oxidation conditions as given in the legend of Fig. 5.3. These curves are for Si(001). Si(111) curves are similar.
Figure 5.5 Capture numbers and coverages determined from the rate equation solution of the dual-species model. The dash of the curves indicates the oxidation conditions as given in the legend. (a) the capture number increases throughout the oxidation as the existing islands grow larger and hence are more efficient at capturing diffusing monomers. (b) The coverage increases linearly in time as a continuous supply of diffusing, back-bonded species attach to the existing islands. The same legend is used for both graphs.
Figure 5.6 Condensation regime terms for various oxidation conditions. Plots result from simulations based on pyrometer temperature readings as discussed in text. The system is entirely within the initially incomplete condensation regime for all oxidation conditions only at low doses.
Figure 5.6 continued.
Figure 5.7 Scaling behavior of stable cluster density with oxidation pressure. The data are from the low dose values as a function of pressure from the Si(001) data shown in Fig. 4.15(a). The best fit slope $\chi = 1.4$ indicates that $i = 2.8$, since the data are in an initially incomplete condensation regime.
Figure 5.8 Experimental example of qualitative scaling on Si(001). Both images are 5000 Å on a side. (a) Oxidation conditions of 640° C, 2x10^-8 torr, and 63 L exposure. (b) Oxidation conditions of 740° C, 1x10^-6 torr, and 63 L exposure. Surface morphologies look practically identical.
CHAPTER 6

DISCUSSION

6.1 Controlling cluster densities

With the dual-species model’s consistency with measured data, the predictive power of the model was then tested. The original goal was to use the kinetic understanding from this model to fabricate ordered arrays of etch structures. Here we would intentionally seed a patterned array of oxide clusters at room temperature with selective H-depassivation. Then an elevated temperature oxidation would be performed which would not locally nucleate any new clusters because diffusing oxygen species would find an existing cluster before nucleating with another diffusing species. In this way, the growth term would dominate from the beginning and the clean areas between the clusters would simply be etched away.

Before beginning these experiments we realized we could test the kinetics of this experiment without actually patterning the clusters on the surface. If we just created some pre-existing density of clusters on the surface then changed the oxidation conditions into a growth only regime we should be able to make arbitrary densities of clusters at arbitrary heights.
The first such experiment to test this idea was to start an oxidation off at 640°C and 6x10^-8 torr where we know that many islands are nucleated quickly. Then before reaching the saturation cluster density at 640°C, but after nucleating more than the saturation density of islands at 690°C, the temperature would be abruptly changed to 690°C. In this way the growth term must dominate, and essentially all diffusing species will find an existing cluster before nucleating a new one. Since the constant vertical etching is continually going on, we may proceed with the oxidation for as long as we wish to etch the clusters higher. The dual-species model's prediction is shown schematically in Fig. 6.1

Figure 6.2 shows the results of this experiment. Figure 6.2(a) shows an STM image of the saturation density of clusters from an oxidation done entirely at 640°C. Figure 6.2(c) shows an STM image of the saturation density of clusters from an oxidation done entirely at 690°C. Finally Fig. 6.2(b) shows clusters densities after the same total oxidation time, but with the first few minutes of the oxidation done at 640°C, then the remainder of the oxidation done at 690°C. For a 3000 Å scan, resulting cluster numbers were 77, 44, and 4 for (a), (b), and (c) respectively. It should also be noted that the uniformity in appearance for the clusters in (b) are strong support that they all nucleated early in the oxidation (at 640°C) and that we could have made them any height we chose by simply extending or decreasing the time spent oxidizing (etching) at 690°C. From a practical standpoint, this uniformity may be quite desirable for the fabrication of ordered arrays of etch structures (possibly an array of field emission tips, for example). From a modeling standpoint, we note that without changing any parameters from those discussed...
in Chapter 5, the quantitative model prediction for the saturation level of this changing temperature experiment was well within a factor of two of the measured experimental cluster density (2.88x10^{10} \text{ cm}^{-2}: \text{predicted}, 4.44x10^{10} \text{ cm}^{-2}: \text{measured}). Furthermore, it is quite possible that additional parameter manipulation could achieve better overall agreement with the experimental data (especially since the largest uncertainty in the fits is at early doses when most all of the islands are nucleating).

Another such experiment that one may try to truly test the model is the converse experiment. In this experiment, the oxidation will start at a high temperature then be lowered to a lower temperature for the remaining time. Naively, one may expect the clusters to nucleate to the same saturation level had the oxidation begun at the lower temperature in the first place. This reasoning, however, is incorrect. As discussed previously, the reason the cluster density saturates in the first place is because a sufficient density of clusters builds-up so as to provide an efficient sink for diffusing oxygen species. To be an effective sink, however, not just the density is important but also the size of the existing clusters. With this being the case then, the model would predict that some large clusters that have been growing for a long time at 690°C should be much more effective sinks than the same number of clusters initially nucleated at 665°C. Therefore, if we decrease the temperature from 690°C to 665°C after some clusters have grown large, the resulting saturation density at 640°C will be less than if we had started at 640°C in the first place. This prediction is shown schematically in Fig. 6.3.

This experiment has also been carried out and the results are shown in Fig. 6.4. In this figure both images are taken in the saturation regime, and the presence of large pre-
existing clusters does in fact clearly reduce the saturation level. In Fig. 6.4(a) the oxidation was done entirely at 665°C for 11764 s, while in Fig. 6.4(b) the oxidation was done first at 690°C for 14892 s, then reduced to the same 665°C oxidation for 11764 s. Clearly the large clusters grown in Fig. 6.4(b) have acted as efficient sinks in suppressing nucleation during the 665°C oxidation, where only 3-5 new islands have appeared to nucleate. Statistical analysis of the heights of islands for many scans taken under such a changing temperature experiment is shown in Fig. 6.5. From this bimodal distribution (and its correspondence with specific islands) it is clear that the laterally smaller islands observed in Fig. 6.4 do in fact have a smaller height consistent with the idea that they nucleated at a later point in time. With the predictive power from these two changing temperature experiments, it appears that the dual-species model could be used to controllably predict the vertical (and potentially even the lateral) evolution of pre-patterned oxide clusters. This type of experiment may involve selective H-depassivation plus subsequent room temperature oxidation to seed the oxide-cluster "masks" as discussed at the beginning of this section, or more conventional nano-scale lithography may be used to seed the oxide clusters. Certainly there are many applications yet to be discovered for this use of oxygen as a simultaneous mask and etchant.

One final test of the model, which has not been pursued, would be to form structures such as those in Fig. 4.13(d), then HF dip the sample to remove the oxide, and then finally re-oxidize the sample in UHV to make sure the surface morphology itself is not affecting the saturation of the oxide cluster density. One problem here would be that the HF dip would be done ex situ and then a thin oxide (and contaminant) layer would
form before placing the sample back into the UHV-STM. This thin layer would have to be removed with a mild anneal so as to maintain as much of the original (rough) morphology as possible. In principle, this experiment can be done and would be an excellent test to see exactly how surface morphology affects (or doesn't affect) oxide cluster nucleation kinetics.

6.2 Height history analysis

If one assumes that the constant vertical etch rate of the surface is laterally uniform as well, then the height of each island essentially tells us when in time that island has nucleated. If this is in fact the case, then in principle, a nucleation history may be built-up from a single STM image by examining the height distributions of islands in the image. An especially suggestive experiment is to try and correlate the height distributions of an oxidation in which oxidation conditions have been changed part way through so that two distinct populations of clusters can be seen. With this type of experiment one would expect that a bimodal height distribution should result, and in fact this has been seen and discussed earlier (Fig 6.5). To perform the height history analysis, a short C program was written to essentially integrate this height distribution, and in doing so, a map was created of the number of clusters as a function of time or dose (Fig. 6.6).

The primary problem with this sort of analysis is quantifying how much information actually gets lost due to the error in measuring the heights of the islands. We
believe this error primarily comes from the uncertainty in determining the appropriate base plane to subtract, but it may be compounded by a spatially non-uniform etch rate. In addition, the offset in time is somewhat unclear because we do not really know when in time the first cluster has nucleated. At first one may suggest taking the tallest island as the “beginning” of time, but it is questionable whether this method is consistent from oxidation to oxidation. In addition, the tallest island may have a false height from one of the common STM “glitches” (i.e. large increases in current and hence heights of features due to a rearrangement of the tip or the sample itself) which commonly occur over oxide patches due to the insulating nature of the material. From our low dose experiments clusters (and assuming a reasonable sticking coefficient of 4%) we believe that the clusters begin to nucleate even before one complete monolayer has been etched, so provided a glitch can be ruled out, this method seems to be acceptable. Using this algorithm then, the data from height distributions shown in Fig 6.5 are plotted in “nucleation history” form in Fig. 6.6. Qualitatively we can see that the general form is consistent with the form predicted by the Monte Carlo simulations of the dual-species model.

Ideally if the error from the base plane subtraction could be removed then we would have a higher confidence as to the accuracy of the measured island heights and we could then begin to try and correlate the shape of the height history curve to the shape predicted by the atomic-scale model in question. The other potential error with this method is that the etching occurring on the surface may not truly be homogeneous within a particular scan area. If etching was enhanced in one area over another then the height of
an island may not be a true indication of when in time it nucleated. Since however, the average island height does increase linearly in time and the height histories do have the correct qualitative form, we can conclude that etching is essentially homogeneous at least on a size scale of the scan size (3000 to 5000 Å). Nevertheless, the shape of the height history curves may be limited by slight spatial inhomogeneities in the etch rate at smaller length scales and hence introduce more error in the determination of the original base plane. Together these errors are difficult if not impossible to quantify and hence limits the usefulness of extracting more specific information from the height history analysis technique.

6.3 The Roughening Regime

6.3.1 Extent with respect to oxidation conditions

The measurements reported here and recent STM measurements reported elsewhere\textsuperscript{66,77} also have interesting implications concerning the critical conditions for SiO\textsubscript{2} growth,\textsuperscript{63,65} shown in Fig. 1.9. Earlier studies done mainly at higher temperatures and with lower spatial resolution indicated a very sharp boundary between the active and passive oxidation regimes, with large-scale surface roughening only occurring over a narrow transition region a few degrees wide.\textsuperscript{65} The more recent atomic resolution studies done at lower temperatures\textsuperscript{76,77,90-94} all indicate that a great deal of surface etching can occur up to \(O_2\) pressures several orders of magnitude above the commonly accepted
"critical line" for passive oxidation, at the same time that oxide clusters nucleate and grow. Consequently, the transition region in which significant atomic-scale surface roughening occurs may actually be much broader than would be expected from the prior measurements. In fact, a recent TEM study has identified a roughening regime under similar conditions on Si(111) which at $P_{ox} = 1 \times 10^{-4}$ torr is as wide as 125 Celsius degrees. Although Ross et al. did not quantify the roughness, they did attribute its origin to simultaneous oxide nucleation and etching resulting in a micromasking process.

Thus the critical line should not be thought of as separating the regions of $P_{ox}/T_s$ space where SiO desorption dominates or oxide growth dominates, because as our experiments and others show, SiO desorption is clearly the dominant reaction (for as long as we have exposed our samples, ~8 hrs) even in a region that will eventually form an oxide film. As Feltz et al. correctly pointed out, the key component that was missing from our original discussion of this phenomenon is time. Eventually at much high doses, the oxide clusters will begin to coalesce and desorption will be suppressed. As a practical matter for device processing, it would be useful to know the range of conditions which produce significant surface roughening on Si(001), and the degree and type of roughness thus produced. Therefore a potentially useful (and ambitious) set of experiments would be to plot out the roughening regime as a function of pressure, temperature, and time. Although by no means complete, the discussion below shows the results of some experiments along these lines.
6.3.2 Quantifying Roughness Evolution

To explore surface roughening within this transition region, we have made measurements of how the rms surface roughness depends on O₂ pressure and temperature. This is done keeping the total O₂ dose constant to ensure that the same amount of oxygen reacts with the surface at each pressure. Figure 6.7 shows results for a 63 L O₂ dose at 640°C. At zero dose (square symbol) the measured rms roughness $\Gamma \approx 0.4$ Å, due mostly to regular steps on the clean vicinal surface. As the O₂ pressure is increased, we see that $\Gamma$ first increases, reaches a maximum near $P_{ox} = 8 \times 10^4$ torr, and thereafter decreases. For pressures below $8 \times 10^4$ torr, the surface is smooth because the etching is essentially layer-by-layer since not many pinning sites (i.e. oxide clusters) have formed. For $P_{ox} > 2 \times 10^7$ torr, STM images invariably show a very smooth, “cloudy” topography, consistent with a very thin, smooth layer of surface oxide. At these higher pressures, a continuous surface oxide forms so quickly that the surface has little chance to etch and roughen. Preliminary measurements indicate that at 740°C, a 63 L dose produced maximum roughening at or above $P_{ox} = 4 \times 10^4$ torr. These two points can be used to draw an approximate line of “maximum roughening” for a 63 L dose, as shown in Fig. 6.8. The position of this line and the peak value of the surface roughness will of course depend on the oxygen dose. The main point here is that substantial atomic-scale surface roughening can occur for conditions well above the accepted critical line. If one is designing a processing sequence for devices which require atomically smooth interfaces, it is
important to avoid these roughening conditions during transient processing steps, i.e., as a substrate is heated or a chamber is vented, etc.

To emphasize the importance of time, Fig. 6.9 shows how the surface roughness evolves with dose. Here it should be noted that now the oxidation pressure and temperature are being held constant and the roughness continues to increase with dose. Given this fact, we have no reason to assume that the "critical line" for maximum roughness at 800 L is the same as the maximum roughening line at 63 L. It would be interesting to do higher pressure experiments at these doses to examine at which pressure the roughness peaks. These experiments would provide us with a better understanding of where passive oxidation begins to takeover the etching reaction.
Figure 6.1 Schematic of a changing oxidation condition experiment as predicted by the dual-species model. In this experiment oxidation starts at 640°C to nucleate many islands quickly, then the temperature is raised to 690°C to abruptly suppress subsequent nucleation.
Figure 6.2 STM images of the changing oxidation conditions experiment depicted in Fig. 6.1. This experiment verifies that nucleation of new clusters may be abruptly suppressed by raising the temperature.
Figure 6.3 Schematic of changing oxidation conditions experiment. In this experiment oxidation starts at 690°C to nucleate a few large clusters, then the temperature is lowered to 665°C to begin to nucleate more clusters. If large pre-existing clusters are efficient sinks for the attachment of diffusing oxygen species then the final saturation density should be lower than if the oxidation was started at the lower temperature in the first place.
Figure 6.4 STM images of changing oxidation conditions experiment depicted in Fig. 6.3. As the dual-species model predicts, large pre-existing clusters do suppress subsequent nucleation.
Figure 6.5 Oxide cluster height distributions with changing oxidation conditions from higher to lower oxidation temperatures. (a)-(d) have been integrated to form a height history shown in Fig. 6.6. For (e) not enough time was spent at 665°C to form a statistically significant population of smaller oxide clusters.
Monte Carlo predictions for 690 → 665°C after various times

Nucleation history based on the average island heights

Figure 6.6 Height History analysis. (a) shows the Monte Carlo predictions of lowering the temperature part-way through an oxidation. (b) shows the integrated number of clusters based on their height (ie. approximately when in time they were nucleated). Qualitatively a trend is present, but quantitative analysis is difficult due to large error introduced in substracting the appropriate base plane as well as possible complication from inhomogenous etching.
Figure 6.7 RMS roughness as a function of oxidation pressure. The peak in the data occurs because passive oxidation eventually takes over the etching reaction at higher pressures. The initial offset to the roughness is due to the vicinal steps on Si(001).
Figure 6.8 Line of maximum roughening at 63 L. This graph suggests that considerable atomic-scale roughening may occur even at pressure-temperature conditions well above the commonly accepted critical line.
Figure 6.9 RMS roughness as a function of dose. This graph emphasizes the fact that maximum roughening conditions must be reported with respect to a specific dose.
CHAPTER 7

CONCLUSION

Silicon oxidation has been examined in a regime in which oxidation-induced etching and oxide cluster nucleation occur simultaneously. This regime has provided a unique opportunity to count individual, nucleated oxide clusters since the nano-masking mechanism accentuates each cluster making it easily countable. For the first time, then, individual oxide clusters have been quantified to directly test atomic-scale kinetic models for silicon oxidation. High dose cluster saturation along with constant vertical etching have shown the single-species oxidation model to be inconsistent with experimental data, while the dual-species oxidation model is consistent.

Cluster nucleation rates have been found to be related to a combination of temperature activated processes. Effective nucleation energies for both Si(001) and Si(111) range from about -3.3 to -4.0 eV. Nucleation rates have also been found to be quite dependent on oxidation pressure, assuring us that the pinning sites observed are in fact due to nucleated oxide clusters. At 640°C and O₂ pressures in the range 10⁻⁸ to 10⁻⁷ torr, the pinning density scales as Pₐₓᵐ (with m ≥ 2), consistent with a kinetic model which requires at least two diffusing oxygen species to nucleate a stable oxide cluster. Additional
pressure and temperature dependence has been used to estimate activation energies and prefactors within the dual-species model. Although most parameters have not been independently measured, where values or limits are known a consistency can be found with the parameters we estimated: $E_d = 3.3 \text{ eV}$, $E_q = 1.0 \text{ eV}$, $E_n = 1.6 \text{ eV}$, $E_g = 1.2 \text{ eV}$, $E_{\text{con}} = E_{\text{con}}^* = 2.8 \text{ eV}$, and $E_s = 2.25 \text{ eV}$. We emphasize that the individual values of these parameters may vary greatly, and that our experimental data could only be used to determine a sum of combined energies, and not the individual energies directly. Nevertheless, with this single set of parameters, this dual-species model has been used to successfully predict the behavior of complex experiments involving changing oxidation conditions and may be used in the future to assist in the controlled growth of nano-scale etch structures.

During the course of these experiments other interesting observations have been made apart from the primary conclusions above. Oxidation of the Si(111)-(7x7) surface in the temperature range 540-640°C is observed to etch the surface, leading to the creation of monolayer-deep holes and the retraction of step edges. Surfaces which are exposed by the etching are often found to reconstruct into metastable 5x5 or 9x9 structures as well as the stable 7x7 structure. These results are consistent with a mobile vacancy model such as that proposed by Bedrossian and Klitsner.

When vicinal Si(001) surfaces are exposed to O$_2$ at $T_s \cong 640°C$ and $P_{ox} \leq 6 \times 10^{-8}$ torr, we observe the preferential retraction of B-type surface steps at low dose ($< 50 \text{ L}$), but complete single A-domain formation is prevented by the pinning of steps by nucleated oxide clusters. By measuring the evolution of these structures with dose, we
estimated surface etching rates and a value of the O\textsubscript{2} sticking coefficients ranging from about 0.033 to 0.053 and as high as 0.084 for high miscut samples.

We also point out that oxygen exposure at these lower temperatures can cause significant atomic-scale surface roughening even up to O\textsubscript{2} pressures several orders of magnitude above the commonly accepted critical line for SiO\textsubscript{2} growth. This roughening is strongly dependent on oxidation pressure and sample temperature. Experiments suggest that conditions for maximum roughening may also depend on the oxidation dose as well.

Finally, more experiments may be done to address some of the outstanding questions. As with any study, almost as many questions are raised as are answered. One such question would be can this knowledge of silicon surface roughening be used to create controllably roughened Si/SiO\textsubscript{2} interfaces for further fundamental study? Interesting aspects here may be electron mobility or enhanced charge trapping. As an experiment to try, Ballistic Electron Emission Microscopy might be used to spatially correlate MOS breakdown voltages underlying nucleated oxide clusters that have been imbedded in a subsequent continuous oxide film. Another interesting question is how do the kinetics of oxidation differ if a different oxidant is used, such as N\textsubscript{2}O? Finally, can patterned etch structures be made by using selective H-depassivation to first seed oxide clusters at room temperature and then exploiting the kinetic understanding of the dual-species oxidation model in the roughening regime? These questions and others could be answered within the next couple of years, and depending on their answers, we may see oxidation kinetics play an ever expanding role in the field of microelectronics.
APPENDIX

Rate Equation Code and Results

This appendix includes the specific code used to run the rate equation simulations for this model. Following the code is a snapshot of the user interface including the standard set of activation energies used throughout the discussion in Chapter 5. Finally, output from the program is given in terms of the magnitude of various terms during the course of an example calculation.
#include <math.h>
#include <float.h>
#include <stdio.h>
#include <stdlib.h>
#include <fcntl.h>
#include <string.h>
#include <ctype.h>
#include <stddef.h>
#include <cx/cxLattice.h>
#include <cx/cxLattice.apiJi>
#include <cx/cxParameter.apiJi>
#include <cx/DataTypes.h>
#include <cx/DataAccessJi>
#include <cx/DataOpsJi>

#ifdefcplusplus
extern "C" {
#endif

void oxMod ( 
    double flux,
    double temp,
    double Ea,
    double Ed,
    double En,
    double Eg,
    double Eb,
    double Ebp,
    double pre_a,
    double pre_d,
    double pre_b,
    double pre_pb,
    double cap,
    int time_2,
    int layers_etched_2,
    int stop_flag,
    int print_flag,
    int run_flag,
    double pressure,
    double sticking,
    unsigned char * filename,
    double etch_rate,
    int flux_flag,
    double time_step,
    int plot_versus,
    double points_out,
    cxLattice ** erlat,

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cxLattice ** stableflat,
  cxLattice ** w1lat,
  cxLattice ** w2lat,
  cxLattice ** w3lat,
  cxLattice ** w4lat,
  cxLattice ** difflengthlat,
  cxLattice ** covlat,
  cxLattice ** isizelat,
  double    time_new1,
  double    time_new2,
  double    pressure_new1,
  double    pressure_new2,
  double    temp_new1,
  double    temp_new2,
  int       step_flag,
  int       surf_flag);

#ifdef cplusplus
}
#endif

void oxMod ( 
  double    flux,
  double    temp,
  double    Ea,
  double    Ed,
  double    En,
  double    Eg,
  double    Eb,
  double    Ebp,
  double    Ebp,
  double    pre_a,
  double    pre_d,
  double    pre_b,
  double    pre_pb,
  double    pre_bp,
  double    cap,
  int       time_2,
  int       layers_etched_2,
  int       stopping,
  int       print_flag,
  int       run_flag,
  double    pressure,
  double    sticking,
  unsigned char * filename,
  double    etch_rate,
  int       flux_flag,
  double    time_step,

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int plotversu,
double points_out,
cxLattice * erlat,
cxLattice * stableflat,
cxLattice * w1lat,
cxLattice * w2lat,
cxLattice * w3lat,
cxLattice * w4lat,
cxLattice * diflengthlat,
cxLattice * covlat,
cxLattice * isizelat,
double time_new1,
double time_new2,
double pressure_new1,
double pressure_new2,
double temp_new1,
double temp_new2,
int step_flag,
int surf_flag
{
FILE *ofp;

double capture, diffgeom, diffreq, descov, desfreq, sites, kb, temperature, Tox, P, mO2, R, diffco, tau;
double desfreq4, tau4;
double desfreq4, tau4;
double monop, monob, stable, atoms, twos, a, b, initn1p, initn1b, initnx, inits, initn2, t, h;
double c1, c2, c3, c4, c5, c6, c7, c8, f, N, w5, Ebreak;
double w1, w2, w3, w4, cov, sigmax, sigmax1, sigmax2, sigmax3, sigmax4, sigmaxf, stablef;
double layers, er, k15, k25, k35, k45;
double k11, k12, k13, k14, k21, k22, k23, k24, k31, k32, k33, k34, k41, k42, k43, k44;
double nuke1, nuke2, tau2, tau3, desfreq2, desfreq3;
double life, diflength, convert, nucleate, add2, grow, isize, N2, dose;
int i, j, N3, done1, done2;
double t_flux, c, des, con1, con2, t_nuc2lose, t_nuc2get, t_breakget, t_breaklose, t_grow, t_nuc2get;

CxParameter * parm;
char indx[10];
char * gfname;
char fname[300];
FILE * tfile;
FILE * gfile;
int fst;
char str[300];

cxLattice * erlat1 = (cxLattice *)NULL;
cxLattice * stableflat1 = (cxLattice *)NULL;
cxLattice * w1lat1 = (cxLattice *)NULL;
cxLattice * w2lat1 = (cxLattice *)NULL;
cxLattice * w3lat1 = (cxLattice *)NULL;
cxLattice * w4lat1 = (cxLattice *)NULL;
cxLattice * diflengthlat1 = (cxLattice *)NULL;
cxLattice * covlat1 = (cxLattice *)NULL;
cxLattice * isizelat1 = (cxLattice *)NULL;

int nDim = 1, nDataVar = 1;
long dims = (long)points_out;

if (plot_versus || 1)
{
erlat1 = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_uniform);
stableflatl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_uniform);
wllatl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_uniform);
w2latl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_uniform);
w3lat1 = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_uniform);
w4latl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_uniform);
diflengthlatl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_uniform);
coviatl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_uniform);
isizelat1 = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_uniform);
}

if (plot_versus == 1)
{
erlat1 = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_perimeter);
stableflatl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_perimeter);
wllatl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_perimeter);
w2latl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_perimeter);
w3lat1 = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_perimeter);
w4latl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_perimeter);
diflengthlatl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_perimeter);
coviatl = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_perimeter);
isizelat1 = cxLatNew(nDim, &dims, nDataVar, cx_prim_float, 1, cx_coord_perimeter);
}

/*
*/
if (surf_flag == 0)
sites = 1.695e6; /* Si(001) monolayer */
else
sites = 3.914876e6; /* Si(111) bilayer */

kb = 8.617e-5;
Tox = 300.0;
mO2 = 5.3137e-26;

initlp = 0.0;
initlb = 0.0;
init2 = 0.0;
initnx = 1.0e-5; /* small but non-zero to avoid divide by 0 error */
initns = 1.0e-5;

R = (pressure*133.0*sticking/(sqrt(2.0*3.1415926*mO2*1.38e-23*Tox))/1.0e20)*5000.0*5000.0;
diffco = pre_d*exp(-Ed/(kb*temp))/sites;
tau = exp(Ea/(kb*temp))/pre_a;
tau2 = exp((Ep)/(kb*temp))/pre_pb;
tau3 = exp((Ebp)/(kb*temp))/pre_bp;

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tau4 = pre_b*exp((-Eb)/(kb*temp));
nuke1 = exp(-En/(kb*temp));
nuke2 = exp(-Eg/(kb*temp));

/* 600 => 2070-3330 and 625 => 1325-1540 */
/* H=2544-3110 M=1020-1333 L=380-502 Deposition Rate */
/* (molecules) per sites per s */

/* AVERAGE VALUES: 600 -> 2146.0 */
/* 625 -> 1500.0 */
/* 650 -> 1234.0 */
/* high -> 2978.0 */
/* low -> 461.50 */

if (flux_flag == 0) cl = flux;
if (flux_flag == 1) cl = (etch_rate*sites)/2;
if (flux_flag == 2) cl = R;

c2 = 1/tau;
c3 = diffco;
c4 = nuke1;
c5 = nuke2;
c6 = 1/tau2; /* desorption precursor -> bridge-bonded */
c7 = 1/tau3; /* bridge-bond -> desorption precursor */
c8 = tau4;

if (run_flag == 1)
{
    printf("%Le = rate
",c1);
    printf("%Le = desorption\n",c2);
    printf("%Le = diffusion\n",c3);
    printf("%Le = nucleation\n",c4);
    printf("%Le = growth\n",c5);
    printf("%Le = pre -> bridgebond\n",c6);
    printf("%Le = bridgebond -> pre\n",c7);
    printf("%Le = breakup\n",c8);
}

...
strcpy(fname, gfname);
sprintf(indx, ",%i", i);
strcat(fname, indx);
if ( (tfile = fopen(fname, "r")) == NULL )
    fst = FALSE;
else
    fclose(tfile);
}

if ( (gfile = fopen(fname,"w")) == NULL )
{
    char str[200];
sprintf(str,"Unable to open file: %s", fname);
    cxModAlert( str );
    return;
}

/*
  /* printf("file = %s,\n",&filename); */
  /* ofp = fopen(&filename, "w"); */
  printf("Ea=%Le\n",Ea);
  printf("Ed=%Le\n",Ed);
  printf("Eb=%Le\n",Eb);
  printf("Ep=%Le\n",Ep);
  printf("Ebp=%Le\n",Ebp);
  printf("En=%Le\n",En);
  printf("Eg=%Le\n",Eg);
  printf("despre=%Le\n",pre_a);
  printf("difpre=%Le\n",pre_d);
  printf("pbpre=%Le\n",pre_pb);
  printf("bppre=%Le\n",pre_bp);
  printf("sigma=%Le\n",cap);
  printf("T=%Le\n",temp);
  printf("P=%Le\n",cl);

if (print_flag == 1)
{
    fprintf(gfile,"0 00000000  %Le\n",Ea);
    fprintf(gfile,"0 00000000  %Le\n",Ed);
    fprintf(gfile,"0 00000000  %Le\n",Eb);
    fprintf(gfile,"0 00000000  %Le\n",Ep);
    fprintf(gfile,"0 00000000  %Le\n",Ebp);
    fprintf(gfile,"0 00000000  %Le\n",En);
    fprintf(gfile,"0 00000000  %Le\n",Eg);
    fprintf(gfile,"0 00000000  %Le\n",pre_a);
    fprintf(gfile,"0 00000000  %Le\n",pre_d);
    fprintf(gfile,"0 00000000  %Le\n",pre_pb);
    fprintf(gfile,"0 00000000  %Le\n",pre_bp);
    fprintf(gfile,"0 00000000  %Le\n",cap);

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fprintf(gfile,"0 0 0 0 0 0 0 0 0 %Le\n", temperature);
fprintf(gfile,"0 0 0 0 0 0 0 0 %Le\n", c1);

/***********************************************************/

b = (sites/(flux*2))*layers_etched_2;
if (stop_flag == 0) b = time_2;
dose = b*pressure/1e-6;
    h = time_step;
    N = b/h;
    N3 = points_out;
    N2 = N/N3;
    t = 0.0;
    w1 = initlp;
    w2 = initlb;
    w3 = init2;
    w4 = initx;
    w5 = init;

if (plot_versus == 0)
    {
* (erlatl->coord->c.cx_coord_uniform.bBox) = 0;
* (erlatl->coord->c.cx_coord_uniform.bBox+1) = (float)b;
* (stableflatl->coord->c.cx_coord_uniform.bBox) = 0;
* (stableflatl->coord->c.cx_coord_uniform.bBox+1) = (float)b;
* (w1latl->coord->c.cx_coord_uniform.bBox) = 0;
* (w1latl->coord->c.cx_coord_uniform.bBox+1) = (float)b;
* (w2latl->coord->c.cx_coord_uniform.bBox) = 0;
* (w2latl->coord->c.cx_coord_uniform.bBox+1) = (float)b;
* (w3latl->coord->c.cx_coord_uniform.bBox) = 0;
* (w3latl->coord->c.cx_coord_uniform.bBox+1) = (float)b;
* (w4latl->coord->c.cx_coord_uniform.bBox) = 0;
* (w4latl->coord->c.cx_coord_uniform.bBox+1) = (float)b;
* (diflengthlatl->coord->c.cx_coord_uniform.bBox) = 0;
* (diflengthlatl->coord->c.cx_coord_uniform.bBox+1) = (float)b;
* (covlatl->coord->c.cx_coord_uniform.bBox) = 0;
* (covlatl->coord->c.cx_coord_uniform.bBox+1) = (float)b;
* (isizelatl->coord->c.cx_coord_uniform.bBox) = 0;
* (isizelatl->coord->c.cx_coord_uniform.bBox+1) = (float)b;
    }
if (plot_versus == 2)

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for (j=0; j<N3+1; j++)
{
    for (i=0; i<N2; i++)
    {
        sigmax1 = 2 + pow(labs(w5/w4), cap);
        monop = 2*c1*(1 - (w5 + 2*w3 + w2 + w1)/sites) - c2*w1 - c6*w1 + c7*w2;
        k11 = h*monop;

        monob = c6*w1 - c7*w2 - 6*c3*c4*w2*w2 - 3.8*c3*c5*w2*w3 + 2*c8*w3 -
               sigmax1*c3*c5*w2*w4;
        k12 = h*monob;

        twos = 3*c3*c4*w2*w2 - c8*w3 - 3.8*c3*c5*w2*w3;
        k13 = h*twos;

        stable = 3.8*c3*c5*w2*w3;
        k14 = h*stable;

        atoms = 11.5*c3*c5*w2*w3 + sigmax1*c3*c5*w2*w4;
        k15 = h*atoms;

        sigmax2 = 2 + pow(labs((w5+0.5*k15)/(w4+0.5*k14)), cap);
        monop = 2*c1*(1 - (w5 + 0.5*k15) + 2*(w3 + 0.5*k13) + (w2 + 0.5*k12) + (w1 + 0.5*k11))/sites) /
\[-c_2(w_1+0.5*k_{11}) - c_6(w_1+0.5*k_{11}) + c_7(w_2+0.5*k_{12});\]
\[k_{21} = h*\text{monop};\]
\[\text{monob} = c_6(w_1+0.5*k_{11}) - c_7(w_2+0.5*k_{12}) - 6*c_3*c_4*(w_2+0.5*k_{12})*(w_2+0.5*k_{12}) - 3.8*c_3*c_5*(w_2+0.5*k_{12})*(w_3+0.5*k_{13}) + 2*c_8*(w_3+0.5*k_{13}) - \text{sigmax2}^2*c_3*c_5*(w_2+0.5*k_{12})*(w_4+0.5*k_{14});\]
\[k_{22} = h*\text{monob};\]
\[\text{twos} = 3*c_3*c_4*(w_2+0.5*k_{12})*(w_2+0.5*k_{12}) - c_8*(w_3+0.5*k_{13});\]
\[k_{23} = h*\text{twos};\]
\[\text{stable} = 3.8*c_3*c_5*(w_2+0.5*k_{12})*(w_3+0.5*k_{13});\]
\[k_{24} = h*\text{stable};\]
\[\text{atoms} = 11.5*c_3*c_5*(w_2+0.5*k_{12})*(w_3+0.5*k_{13}) + \text{sigmax2}^2*c_3*c_5*(w_2+0.5*k_{12})*(w_4+0.5*k_{14});\]
\[k_{25} = h*\text{atoms};\]
\[\text{sigmax3} = 2 + \text{pow(labs((w_5+0.5*k_{25}))/(w_4+0.5*k_{24})),cap);\]
\[\text{monop} = 2*c_1*(1-((w_5+0.5*k_{25})+2*(w_3+0.5*k_{23})+(w_2+0.5*k_{22})+(w_1+0.5*k_{21}))/\text{sites}) - c_2*(w_1+0.5*k_{21}) - c_6*(w_1+0.5*k_{21}) + c_7*(w_2+0.5*k_{22});\]
\[k_{31} = h*\text{monop};\]
\[\text{monob} = c_6*(w_1+0.5*k_{21}) - c_7*(w_2+0.5*k_{22}) - 6*c_3*c_4*(w_2+0.5*k_{22})*(w_2+0.5*k_{22}) - 3.8*c_3*c_5*(w_2+0.5*k_{22})*(w_3+0.5*k_{23}) + 2*c_8*(w_3+0.5*k_{23}) - \text{sigmax3}^2*c_3*c_5*(w_2+0.5*k_{22})*(w_4+0.5*k_{24});\]
\[k_{32} = h*\text{monob};\]
\[\text{twos} = 3*c_3*c_4*(w_2+0.5*k_{22})*(w_2+0.5*k_{22}) - c_8*(w_3+0.5*k_{23});\]
\[k_{33} = h*\text{twos};\]
\[\text{stable} = 3.8*c_3*c_5*(w_2+0.5*k_{22})*(w_3+0.5*k_{23});\]
\[k_{34} = h*\text{stable};\]
\[\text{atoms} = 11.5*c_3*c_5*(w_2+0.5*k_{22})*(w_3+0.5*k_{23}) + \text{sigmax3}^2*c_3*c_5*(w_2+0.5*k_{22})*(w_4+0.5*k_{24});\]
\[k_{35} = h*\text{atoms};\]
\[\text{sigmax4} = 2 + \text{pow(labs((w_5+0.5*k_{35}))/(w_4+0.5*k_{34})),cap);\]
\[\text{monop} = 2*c_1*(1-((w_5+0.5*k_{35})+2*(w_3+0.5*k_{33})+(w_2+0.5*k_{32})+(w_1+0.5*k_{31}))/\text{sites}) - c_2*(w_1+0.5*k_{31}) - c_6*(w_1+0.5*k_{31}) + c_7*(w_2+0.5*k_{32});\]
\[k_{41} = h*\text{monop};\]
\[\text{monob} = c_6*(w_1+0.5*k_{31}) - c_7*(w_2+0.5*k_{32}) - 6*c_3*c_4*(w_2+0.5*k_{32})*(w_2+0.5*k_{32});\]
\[-3.8c_3c_5(w_2+0.5k_22)(w_3+0.5k_23) + 2c_8(w_3+0.5k_33)\]
\[-\text{Sigmax}4c_3c_5(w_2+0.5k_32)(w_4+0.5k_34)\]

\[k_{42} = h\text{monob} ;\]
\[\text{twos} = 3c_3c_4(w_2+0.5k_32)(w_2+0.5k_32) - c_8(w_3+0.5k_33)\]
\[-3.8c_3c_5(w_2+0.5k_32)(w_3+0.5k_33)\]

\[k_{43} = h\text{twos} ;\]
\[\text{stable} = 3.8c_3c_5(w_2+0.5k_32)(w_3+0.5k_33) ;\]
\[k_{44} = h\text{stable} ;\]
\[\text{atoms} = 11.5c_3c_5(w_2+0.5k_32)(w_3+0.5k_33)\]
\[+\text{Sigmax}4c_3c_5(w_2+0.5k_32)(w_4+0.5k_34)\]
\[k_{45} = h\text{atoms} ;\]

\[w_1 = w_1 + (k_{11} + 2k_{22} + 2k_{31} + k_{41})/6 ;\]
\[w_2 = w_2 + (k_{11} + 2k_{22} + 2k_{32} + k_{42})/6 ;\]
\[w_3 = w_3 + (k_{13} + 2k_{23} + 2k_{33} + k_{43})/6 ;\]
\[w_4 = w_4 + (k_{14} + 2k_{24} + 2k_{34} + k_{44})/6 ;\]
\[w_5 = w_5 + (k_{15} + 2k_{25} + 2k_{35} + k_{45})/6 ;\]
\[\text{er} = (c_2w_1)/(\text{sites}-w_5) ;\]
\[\text{layers}+ = h \times \text{er} ;\]
\[t+ = h ;\]

if (step_flag != 0) {
if ((t >= time_new1) && (done1 == 0)) {
R = (pressure_new1*133.0*sticking/(sqrt(2.0*3.1415926*mO2*1.38e-23*Tox))/1.0e20)*5000.0*5000.0;
    diffco = pre_d*exp(-Ed/(kb*temp_new1))/sites;
    tau = exp(Ea/(kb*temp_new1))/pre_a;
    tau2 = exp(Ebpb/(kb*temp_new1))/pre_pb;
    tau3 = exp((Ep)/(kb*temp_new1))/pre_bp;
    tau4 = pre_b*exp((-Eb)/(kb*temp_new1));
    nuke1 = exp(-En/(kb*temp_new1));
    nuke2 = exp(-Eg/(kb*temp_new1));
    c2 = 1/tau;
    c3 = diffco;
    c4 = nuke1;
    c5 = nuke2;
    c6 = 1/tau2; /* desorption precursor -> bridge-bonded */
    c7 = 1/tau3; /* bridge-bond -> desorption precursor */
    c8 = tau4;
    done1 = 1;
}

if (step_flag == 2) {
if ((t >= time_new2) && (done2 == 0)) {
R = (pressure_new2*133.0*sticking/(sqrt(2.0*3.1415926*mO2*1.38e-23*Tox))/1.0e20)*5000.0*5000.0;
    diffco = pre_d*exp(-Ed/(kb*temp_new2))/sites;
}

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\[
\begin{align*}
tau &= \exp(Ea/(kb*temp_new2))/pre_a; \\
tau2 &= \exp((Eb)/(kb*temp_new2))/pre_pb; \\
tau3 &= \exp(Eb/(kb*temp_new2))/pre_bp; \\
tau4 &= pre_b*\exp((-Eb)/(kb*temp_new2)); \\
nuke1 &= \exp(-En/(kb*temp_new2)); \\
nuke2 &= \exp(-Eg/(kb*temp_new2));
\end{align*}
\]
\[
c2 = 1/tau; \\
c3 = diffco; \\
c4 = nuke1; \\
c5 = nuke2; \\
c6 = 1/tau2; /* desorption precursor -> bridge-bonded */ \\
c7 = 1/tau3; /* bridge-bond -> desorption precursor */ \\
c8 = tau4; \\
done2 = 1;
\]
\[
\text{printf("%Le %Le %Le", time_new2, temp_new2, pressure_new2);} \\
}\}
\] /* end of inner loop (i) */

\[
sigmaxf = 2 +\text{pow(labs(w5/w4),cap);} \\
stablef = 3.8*c3*c5*w2*w3; /*nucleation rate */
\]
\[
life = 1 / (c7); /* +6*c3*c4*w2 + 3.8*c3*c5*w3 + sigmaxf*c3*c5*w4); */
\]
diflength = sqrt(c3 * 5000.0 * 5000.0 * life); /* in angstroms since c3 is per scan */

convert = c7;
\[
nucate = 6*c3*c4*w2; \\
add2 = 3.8*c3*c5*w3; \\
grow = sigmaxf*c3*c5*w4;
\]

/*
\[
t = (((j+1) * N2) * h); /*
\]

isize = w5/w4; 
\[
\text{cov = w5 / sites; /* Actually layers etched */}
\]

/* tracking values */

\[
t_{\text{flux}} = 2*c1*(1-(w5+2*w3+w2+w1)/sites); \\
t_{\text{des}} = c2*w1; \\
t_{\text{con1}} = c6*w1; \\
t_{\text{con2}} = c7*w2; \\
t_{\text{nuc2lose}} = 6*c3*c4*w2*w2; \\
t_{\text{nuc2s}} = 3.8*c3*c5*w2*w3; \\
t_{\text{breakget}} = 2*c8*w3; \\
t_{\text{breaklose}} = c8*w3; \\
t_{\text{grow}} = sigmaxf*c3*c5*w2*w4; \\
t_{\text{nuc2get}} = 3*c3*c4*w2*w2;
\]
if (print_flag == 1) {
    fprintf(gfile, "%Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le
%Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le
%, layers, st, w1, w2, w3, w4, difflength, cov, isize, sigmaxf, t_flux, t_des, t_con1, t_con2, t_nuc2lose, t_nuc2get, t_breakget, t_breaklose, t_grow, t_nuc2get);
}

printf("%Le %Le %Le %Le %Le %Le %Le %Le %Le %Le %Le
", layers, er, stable, w1, w2, w3, w4, difflength, cov, isize);

*(erlatl->data->d.cx_prim_float.values + j) = (float) er;
*(stableflatl->data->d.cx_prim_float.values + j) = (float) stable;
*(w1latl->data->d.cx_prim_float.values + j) = (float) w1;
*(w2latl->data->d.cx_prim_float.values + j) = (float) w2;
*(w3latl->data->d.cx_prim_float.values + j) = (float) w3;
*(w4latl->data->d.cx_prim_float.values + j) = (float) w4;
*(difflengthlatl->data->d.cx_prim_float.values + j) = (float) difflength;
*(covlatl->data->d.cx_prim_float.values + j) = (float) cov;
*(isizelatl->data->d.cx_prim_float.values + j) = (float) isize;

if (plotversus == 1) {
    *(erlatl->coord->c.cx_coord_perimeter.perimCoord+j) = (float) layers;
    *(stableflatl->coord->c.cx_coord_perimeter.perimCoord+j) = (float) layers;
    *(w1latl->coord->c.cx_coord_perimeter.perimCoord+j) = (float) layers;
    *(w2latl->coord->c.cx_coord_perimeter.perimCoord+j) = (float) layers;
    *(w3latl->coord->c.cx_coord_perimeter.perimCoord+j) = (float) layers;
    *(w4latl->coord->c.cx_coord_perimeter.perimCoord+j) = (float) layers;
    *(difflengthlatl->coord->c.cx_coord_perimeter.perimCoord+j) = (float) layers;
    *(covlatl->coord->c.cx_coord_perimeter.perimCoord+j) = (float) layers;
    *(isizelatl->coord->c.cx_coord_perimeter.perimCoord+j) = (float) layers;
}

fclose(gfile);

/* end of outer loop (j) */

fclose(gfile);

/* for (j=1; j<10; ++j)
    printf("%Le\n", erlat->data->d.cx_prim_float.values[j]);
*/

* erlat = (cxLattice *) NULL;
* stablelat = (cxLattice *) NULL;
* w1lat = (cxLattice *) NULL;
* w2lat = (cxLattice *) NULL;
* w3lat = (cxLattice *) NULL;
* w4lat = (cxLattice *) NULL;

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* diflengthlat = (cxLattice *) NULL;
* covlat = (cxLattice *) NULL;
* isizelat = (cxLattice *) NULL;

* erlat = erlatl;
* stableflat = stableflat1;
* w1lat = w1lat1;
* w2lat = w2lat1;
* w3lat = w3lat1;
* w4lat = w4lat1;
* diflengthlat = diflengthlat1;
* covlat = covlat1;
* isizelat = isizelat1;

)
Figure A.1 User interface for the dual-species model rate equation code.
Figure A.2 Term magnitudes from a representative run of the dual-species model’s rate equation calculations. At early doses the loss of nucleating species is dominated by the loss to desorption (which is just conversion back to the desorption precursor state). At higher doses, the loss to growth takes over. This is why the condensation regime is initially incomplete, consistent with Fig. 6.5.
LIST OF REFERENCES


64 C. Gelain, A. Cassuto, and P. Le Goff, Ox. Metals 3, 139 (1971).

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