INTERACTIONS OF ATOMIC OXYGEN WITH Pt(111) AND NITRIDED Si(100)

By

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This dissertation is dedicated to my late grandfather, Delbert Barrow.
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INTERACTIONS OF ATOMIC OXYGEN WITH Pt(111) AND NITRIDED Si(100)

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Gas-phase oxygen atoms play a critical role in several applications including degradation of materials in low Earth orbits, semiconductor processing, and heterogeneous catalysis. In each of these applications, the highly reactive nature of the oxygen atom dictates the details of the oxygen atom-surface reactions. Whether the goal is to develop new materials resistant to oxidation or to use the oxygen atoms to generate surfaces with unique properties, a fundamental understanding is needed of the chemistry governing the interactions of O-atoms with surfaces.

Silicon nitride is used in applications because it resists oxidation. We conducted an X-ray photoelectron spectroscopy (XPS) study to examine the surface chemistry of nitrided Si(100) toward molecular and atomic oxygen. A decrease was observed in the Si(100) surface dangling bond density due to nitridation, and this was accompanied by a subsequent decrease in surface reactivity for both molecular and atomic oxygen. This
indicates that oxygen atoms preferentially react at these dangling bond sites, and do not insert directly into silicon-silicon bonds.

Using mass spectrometry, we explored the reactivity of gaseous $^{16}$O-atoms toward chemisorbed $^{18}$O$_2$ on the Pt(111) surface. The gas-phase oxygen atoms stimulate both displacement and dissociation of adsorbed $^{18}$O$_2$. As the surface temperature increased, the desorption yield decreased, with the balance remaining on the surface in the form of chemisorbed atoms. Molecular oxygen is known to adsorb in superoxo and peroxo configurations on Pt(111). The strong temperature dependence on the dissociation yield is attributed to an increase in the population of the peroxo chemisorbed species with temperature, which is more prone to dissociate.

Platinum is catalytically active toward the oxidation of CO. Using O$_2$ under ultrahigh vacuum conditions, a maximum surface coverage of 0.25 monolayers (ML) of O-atoms can be generated. Surfaces with higher oxygen coverages can be generated by exposing Pt(111) to oxygen atoms. Using mass spectrometric methods, an *in situ* CO oxidation study was conducted on these surfaces. The CO oxidation kinetic behavior was found to be consistent with a CO adsorption precursor model. Carbon monoxide oxidation on platinum oxide occurs predominately at the interface between the metallic regions and the oxide.
CHAPTER 1
INTRODUCTION

1.1 Research Objective

Our main objective was to develop a fundamental understanding of interactions between oxygen atoms and technologically relevant surfaces. Oxygen atoms are present in semiconductor plasma processes and in low Earth orbits. These radicals are known to be significantly more reactive than their molecular counterpart. It is believed that O-atom chemistry plays an important role in semiconductor processes, polymer erosion, and low pressure metal oxide formation. Conducting well characterized O-atom beam experiments on metal and semiconductor surfaces provides insight into the underlying chemistry in these areas.

Silicon nitride and oxynitride films have been studied extensively in recent years because of the advantages afforded by incorporating these materials in the dielectric layers used in metal-oxide-semiconductor (MOS) devices. Adding small amounts of nitrogen to the SiO\textsubscript{2}-Si interface is known to improve the structural quality of the interface, and results in lower leakage current across the gate of a MOS device as well as enhanced resistance to boron diffusion into the SiO\textsubscript{2} [1]. The low activity of silicon nitride toward oxidation has also proved beneficial to the growth of alternative gate oxides such as Ta\textsubscript{2}O\textsubscript{5} and ZrO\textsubscript{2} that have higher dielectric constants (k) than SiO\textsubscript{2}. Recent studies show that depositing high k oxides directly onto silicon can result in formation of an SiO\textsubscript{2} layer that dominates the capacitance of the gate stack [2-6]. Incorporating nitrogen in the near-surface region of silicon alleviates this problem by
inhibiting SiO₂ formation during the deposition of Ta₂O₅, thereby maximizing the benefits of the high k oxide film [3,7,8]. Another important application of silicon nitride is as a protective coating on ceramic components such as bearings and turbine blades for which tolerance to high temperature oxidizing environments is critical. Despite these important applications, however, the oxidation of silicon nitride films is not well understood at the molecular level. We studied the oxidation of a silicon nitride film by both gaseous atomic and molecular oxygen in ultrahigh vacuum (UHV), focusing our efforts on elucidating the fundamental origin of the oxidation resistance of nitrided silicon. X-ray photoelectron spectroscopy (XPS) was conducted before and after thermally decomposing nitrogen on the Si(100) surface. The nitrided surface was then exposed to a beam of molecular or atomic oxygen. Changes in the surface due to the oxidant beam were characterized by XPS.

Platinum is considered an important oxidation catalyst in several oxidation reactions. One of the first steps in understanding heterogeneous catalysis on platinum is to learn about the molecular level oxygen interactions with this metal. The Pt(111) crystal face was selected for these studies because of the vast literature characterizing the interactions of molecular oxygen with this surface [9-15]. Molecular oxygen is known to physisorb onto Pt(111) at 20 K. When the surface is heated to 38 K, the molecular oxygen becomes chemisorbed, and generates a saturation coverage of 0.44 monolayers (ML) [11,14]. On heating the sample to 130 K, a competitive process occurs between dissociation and desorption of molecular oxygen, yielding a surface saturated with O-atoms at a coverage of 0.25 ML. The oxygen atoms become mobile on the surface at about 200 K, forming islands with a p(2x2) structure [14]. On continued heating, the
atoms recombine and desorb at about 710 K. The atomic oxygen coverage does not increase beyond 0.25 ML due to the limiting O₂ flux imposed under vacuum conditions. Our study used a beam consisting of atomic and molecular oxygen, and it is useful to characterize the surface behaviors of O-atom radicals with molecular oxygen on Pt(111).

Oxygen atom impingement onto a Pt(111) surface saturated with molecular oxygen has been investigated previously [16,17]. Using isotopically labeled ¹⁸O₂ adsorbed on the surface and gas-phase ¹⁶O-atoms, the displacement of ¹⁸O₂ from the surface and the formation of ¹⁸O¹⁶O was observed at a surface temperature of 80 K. The displacement phenomenon was also observed when directing nitrogen and hydrogen atoms at the ¹⁸O₂ covered surface. Employing time-of-flight mass spectrometry, the desorbing molecules were observed to have a bimodal energy distribution [17]. This was found to be independent of the adsorbing atom. The lower energy desorption component is consistent with thermal evolution of ¹⁸O₂ from the surface. The high-energy desorption feature is direct evidence that some energy from the adsorbing atom is transferred directly into the ¹⁸O₂ before it desorbs. By probing the role of surface temperature, deeper insights into the nature of these phenomena may be found. Intuitively, one would anticipate an increase in the surface temperature would amplify the thermal desorption rate. In our study, we measured molecular oxygen displacement by impinging oxygen atoms as a function of the surface temperature. We also characterized oxygen uptake caused by impinging oxygen atoms. The adsorbed ¹⁸O₂ was not found to be displaced by gas-phase ¹⁶O₂, and hence no ¹⁶O₂ adsorbed onto the surface. Any ¹⁶O-atoms found on the surface must, therefore, originate from the ¹⁶O-atoms in the beam.
Platinum is considered an active oxidation catalyst in many areas [18-20]. Along with probing oxygen atom-adsorbate reactivity, oxygen atoms can generate high coverages of adsorbed oxygen atoms on Pt(111), previously unattainable using molecular oxygen in UHV (0.25 ML). Carbon monoxide oxidation on Pt(111) has been studied in detail with oxygen coverages (θO) on the order of 0.25 ML [8,21-40]. This makes CO an excellent probe molecule for characterizing the relative reactivity of the high-coverage phases of oxygen atoms on Pt(111). Interestingly, this also presents an opportunity to perform molecular-level experiments on catalytic surfaces that can be generated under high-pressure reaction systems. In the experiments presented in chapter four, surfaces with high oxygen atom coverages were generated by exposing clean Pt(111) to an oxygen atom beam. This surface was then exposed to a CO beam while holding the surface temperature constant and monitoring the background partial pressure of CO₂ using a mass spectrometer. Temperature programmed desorption spectroscopy (TPD) was performed after each beam experiment to quantify the products remaining on the surface.

Next, I discuss gas-surface reaction mechanisms and the nature of O-atom interactions with Si(100) and Pt(111). To conduct such experiments, a UHV chamber was constructed and equipped with all of the equipment necessary to conduct the spectroscopic measurements described above. The system and its capabilities are described in Section 1.3.

1.2 Literature Search

1.2.1 Reaction Mechanisms

The studies presented here entail characterizing the reactivity of oxygen atoms with surfaces and characterizing the surface changes caused by the gas phase O-atom. The
free radical nature of the oxygen atom suggests that any oxygen atom-adsorbate interactions will rapidly occur and should not be dependent on surface temperature. Characterizing these surfaces with a probe molecule (such as CO), TPD, or temperature programmed reaction (TPR) requires a sound understanding of thermal reaction chemistry occurring on solid surfaces. Three distinct mechanisms describing surface reactions are discussed here.

A classical description of a thermal heterogeneous catalytic reaction is the Langmuir-Hinshelwood (LH) mechanism. To show how this mechanism works, consider the surface reaction $A + B \rightarrow AB$. First, both species $A$ and $B$ thermally accommodate to the surface. At sufficiently high surface temperatures, these species become mobile and diffuse across the surface. Once the reactants find each other and if they have enough energy to overcome the activation energy for reaction, they will react to form $AB$. Finally, $AB$ desorbs from the surface (Figure 1-1).

Gas-phase oxygen atoms are highly reactive, and any interaction between this species and adsorbates or surfaces should not depend on surface temperature. It is then useful to understand fundamental nonthermal reaction mechanisms; the simplest is the Eley-Rideal (ER) mechanism. This mechanism is shown in the following reaction steps. First, one of the components ($A$) thermally accommodates with the surface. An oncoming $B$ particle collides with $A$ in a single collision and they react to form $AB$. A portion of the reaction energy between $A$ and $B$ is transferred into the kinetic energy of the product molecule, allowing $AB$ to immediately desorb (Figure 1-1). This energy could be transferred into the nuclear motion of the products (the translational, vibrational, and rotational modes), which allows the reaction products to desorb in a directed manner.
Note that this reaction has a very small cross-section, because B must strike A in the first collision, otherwise the B would either back scatter or stick to the surface.

Alternatively, a nonthermal reaction may occur via the hot atom (HA) mechanism. The HA mechanism is very similar to the ER mechanism, and proceeds in the following manner. First, A thermally accommodates to the surface. Particle B then collides with the surface and becomes trapped, but not thermally accommodated to the surface. After several B-surface collisions, the B then collides with A and reacts to form AB. The product AB then immediately desorbs from the surface (Figure 1-1). Since the B particle is trapped at the surface, it may collide frequently with the surface, increasing the probability that B will react with A. This causes the cross-section for the reaction by the HA mechanism to be higher than that of the ER mechanism.

The ER and HA mechanisms have distinct kinetic features, that are observed as the reaction products are monitored. Using oxygen atoms as the highly reactive “B” species, the ER mechanism should have a reaction cross-section similar to that of the atomic dimensions ($10^{-16}$ cm$^2$). The rate for the ER mechanism is given by the expression $R = \Phi \sigma \Theta$, where $\Phi$ is the flux of gaseous oxygen atoms at the surface, $\sigma$ is the reaction cross-section, and $\Theta$ is the adsorbate surface concentration. In this mechanism, the product formation rate would first begin at the maximum, and then decay exponentially to the baseline. Through quantitative analysis of the rate data, the HA mechanism can be distinguished from the ER mechanism in the following ways. The HA mechanism may have a substantially larger cross-section because of the multiple atom-surface collisions that occur before the reaction [41,42]. This also generates a surface concentration of these hot atoms on the substrate, which can influence the kinetics. For example, if sites
are available on the surface before the reaction, the probability of an O-atom sticking in an available site will compete with the probability of reacting with an adsorbed product A. This will yield a time delay before the rate maximum, which has been observed when H-atoms were directed toward surfaces coated with D-atoms [42,43]. Additionally, unanticipated products may form when the HA mechanism dominates the nonthermal chemistry. While directing hydrogen atoms onto deuterium-covered metal surfaces, Kammler et al. [42,43] observed the formation of HD and D₂. The homo-isotopic product was attributed to the generation of secondary hot D-atoms. Secondary hot atom formation has been observed in a number of studies for gaseous H-atoms reacting with adsorbates [41,44-47] and can be detected by isotopically labeling the adsorbate molecule.

1.2.2 Molecular and Atomic Oxygen Interactions with Si(100)

Although UHV studies on the oxidation of silicon nitride films are sparse, oxidation of single crystal silicon surfaces has been studied extensively. Of particular relevance to our study are detailed UHV studies by Engstrom et al. [48] on the oxidation Si(100) and Si(111) by both gaseous atomic and molecular oxygen. These and other results were discussed by Engel [49] in a review of Si oxidation. Briefly, under UHV conditions, the dissociative adsorption of O₂ on Si(100) yields effective saturation coverage of only about 1 ML of oxygen atoms when the surface is held at 300 K during oxidation. The saturation coverage can be increased by oxidizing in UHV at elevated surface temperature, but the oxygen uptake is still rather limited. For example, the saturation oxygen coverage increases to 2 ML when Si(100) is exposed to O₂ at a surface temperature of 800 K. Not surprisingly, Engstrom et al. [48] found that gaseous oxygen atoms adsorb on Si(100) with much higher probability than does O₂, and that oxygen
coverages greater than 10 ML can be obtained by oxidizing Si(100) held at 300 K using an atomic oxygen beam. Unlike results obtained using O₂, the uptake of oxygen atoms was insensitive to the surface temperature for oxygen coverages up to about 5 ML, which indicates non-activated adsorption and possibly direct insertion of gaseous O-atoms into surface Si-Si bonds.

1.2.3 Molecular and Atomic Oxygen Interactions with Pt(111)

Molecular oxygen interactions with Pt(111) have been studied extensively, and at 100 K O₂ is known to chemisorb onto the Pt(111) surface, generating a saturation coverage of 0.44 ML [11,14]. As the surface is heated to 140 K, a competitive process between desorption and dissociation occurs. What remains after this process is a platinum surface saturated with oxygen atoms (0.25 ML). These oxygen atoms become mobile at about 200 K, and organize into islands with a p(2x2) structure, with the O-atoms residing in the FCC hollow site. When the sample temperature reaches ~710 K, the adsorbed oxygen atoms recombine and desorb [9-15]. Higher surface coverages of oxygen atoms have been formed by electron dissociation of O₂/Pt(111) [9,50], and exposing Pt(111) to NO₂ [51-53], O₃ [54,55], and gaseous O-atoms [56]. Our research group successfully generated oxygen-atom coverages up to 2.9 ML on Pt(111) with a beam consisting of molecular and atomic oxygen. Oxygen atom uptake and the resulting high O-atom coverage phases on Pt(111) were examined using X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (ELS), low energy electron diffraction (LEED), and TPD.

As the surface coverage of oxygen on the Pt(111) surface exceeds 0.25 ML, the onset of O₂ desorption shifts to lower temperatures during TPD [51,55]. Two distinct
low-temperature desorption features were observed at about 550 and 640 K. Parker et al. [51] attributed this to strong repulsive interactions among neighboring oxygen atoms as well as O-atoms adsorbed in weakly bound hcp hollow sites. As the coverage increases beyond 0.75 ML, the intensity of the low temperature desorption features decrease. Accompanying this observation is the formation of a single sharp desorption peak that shifts to higher temperatures with increasing $\theta_O$. Using XPS and ELS measurements in conjunction with TPD in our laboratory, this sharp desorption feature is attributed to the presence of oxide islands forming on the surface.

1.3 Experimental System

Probing the oxygen atom-surface reactivity at the molecular level required the construction of an ultrahigh vacuum chamber with the capability of monitoring gas phase species and surface properties. A calibrated beam system was designed to create uniform adlayers on the surface and to conduct isothermal reaction rate measurements. To generate the atomic oxygen beams used in these studies a microwave plasma source was employed. The plasma source was inserted into a chamber with two stages of differential pumping to maintain UHV during the plasma operation. Oxygen atoms can react with adsorbed species both on the sample and the chamber walls, which could influence the measurements during the beam experiments. This was addressed by designing a set of collimating apertures for the differentially pumped beam chamber, which minimized the pressure rise in the UHV chamber and focused the beam onto the sample.

1.3.1 The UHV Chamber

The experiments were conducted in a three-level UHV chamber (Figure 1-2) that reaches a base pressure less than $2 \times 10^{-10}$ Torr. The chamber is evacuated by an ion pump (400 L/sec), a turbo molecular pump (210 L/sec), and a titanium sublimation pump
that is inserted into a liquid nitrogen cooled cryoshield. The upper level of the chamber (Figure 1-3) houses a hemispherical analyzer (Specs EA10 plus), a dual Al/Mg anode X-ray source (Specs XR-50), a variable-energy electron source (Specs EQ 22/35) and an ion sputter source (Specs IQE 11), for performing XPS, Auger electron spectroscopy (AES), ELS and low energy ion scattering spectroscopy (LEISS) as well as surface cleaning by ion sputtering. The middle level of the chamber is designed primarily for gas-dosing, and contains a directed doser connected to a leak valve as well as a calibrated molecular beam doser, the design of which closely follows that described by Yates [57]. The lower level of the chamber (Figure 1-3) houses low-energy electron diffraction (LEED) optics, a two-stage differentially-pumped plasma beam source, and a quadrupole mass spectrometer (QMS).

1.3.2 Sample Manipulator

A custom-designed sample manipulator (McAllister Technical Services) was mounted to the top of the UHV chamber. Sample motion in all three Cartesian directions and rotation by 360° about the vertical axis were accomplished using an XY translator, a single-axis translator and a rotary platform. The specimen holder mounts to a copper reservoir that is brazed to the bottom of a stainless steel tube. The top end of the tube mounts onto the rotary platform via a flange with multiple feedthroughs for attaching thermocouples and power wires to the sample. A flat copper plate protrudes from the bottom of the copper reservoir and L-shaped copper legs are bolted on each side of the plate, with sapphire spacers providing electrical isolation between the reservoir and the copper legs (Figure 1-4). The copper legs are each 0.25” wide, extend 2” below the bottom of the copper plate, and are separated from one another by a distance of 1.12”. A specimen is mounted to the sample holder either by directly clipping each side of the
specimen to Ta plates that are bolted to the front of the flat copper legs, or by spot-welding wires to both the specimen and the Ta plates. The Ta plates are in thermal contact with the copper reservoir and can be cooled to temperatures as low as 80 K when the reservoir is filled with liquid nitrogen.

1.3.3 Sample Temperature Control

Accurate temperature control is required during the experiments and to conduct TPD measurements. The following PID control scheme was used for this purpose and is depicted in Figure 1-5. Sample heating is performed resistively by passing current through the sample and the surface temperature is measured with a K-type thermocouple attached to the back of the specimen. The heating current is generated by a Sorenson DCS 33-33 DC power supply, and the sample temperature is regulated using an Omega cn 1166 PID controller. This particular controller has a recorder and controller output. The controller output is wired into the analog control input on the Sorenson power supply. A computer records the output utilizing the analog input port located on the mass spectrometer.

One requirement for analyzing TPD data accurately is the ability to generate a linear temperature ramp. Typically, the heating ramp consists of two components: an initial nonlinear transient component, followed by a linear ramp. The temperature controller must be tuned to maximize the linear region of the ramp and minimize the duration of the transient features. Figure 1-6 shows a typical heating curve for a 1 K/sec ramp rate.

A concern with this heating configuration is that the specimen mount may be damaged when applying current to the sample. This can be minimized if the following
suggestions are followed. Occasionally, the power supply or controller will malfunction and send a power spike across the sample, when initially activated. To avoid this, open the switch in the high current circuit (Figure 1-5) before activating the power supply or controller. When manually changing the set-point, it is safe to rapidly decrease the temperature. However, if the set-point is rapidly increased, even if the actual temperature is 100 °C higher than the set-point, the controller may deliver enough current across the sample to damage the mount. If a temperature ramp is desired, it is imperative to initiate the ramp while the set-point is within 10 °C of the measured temperature.

1.3.4 Beam Chamber

A two-stage differentially-pumped chamber containing a commercial plasma source (Oxford Scientific Instruments) is attached to the UHV chamber and was used to maintain ultrahigh vacuum conditions in the main chamber while operating the plasma source (Figure 1-7). Gaseous oxygen atoms are produced in this system by dissociating O₂ in a plasma that is confined to a small reservoir at the end of the plasma source. The plasma source operates at a microwave frequency (2.45 GHz) and employs electron cyclotron resonance to increase the plasma density. The plasma reservoir is fabricated from high purity alumina to minimize atom recombination and is terminated by a 2 mm thick alumina plate that has five thru holes, each of 0.4 mm diameter, that are arranged in a centered-(2x2) pattern within a 2 mm area. Species exit the plasma volume through these holes, and form a beam that is directed toward the sample surface held in the UHV chamber.

In the first pumping stage, the beam passes between oppositely charged parallel plates (±10 kV/cm) that deflect ions and electrons from the beam path. After flowing through a conical skimmer (φ = 3 mm) separating the first and second pumping stages,
the gas travels down a quartz tube before entering the UHV chamber. The quartz tube is
60 mm long and has an inner diameter of 6 mm. The quartz tube provides a lower
conductance between the source and UHV chambers than would be obtained with a thin-
walled orifice of the same diameter. The quartz tube also provides sufficient collimation
to confine the beam to the sample surface, which facilitates reactive scattering
measurements using mass spectrometry. In addition, collisions at the inner walls of the
tube are expected to reduce the fraction of atoms and molecules in vibrationally and
electronically excited states, which should result in beams containing primarily ground
state species, specifically O(3P) and O2(3Σg−). The first pumping stage of the beam
chamber is evacuated with a 1200 L/sec diffusion pump (Varian VHS 4) and the second
stage is evacuated with a 70 L/sec turbo molecular pump and a titanium sublimation
pump mounted inside a liquid-nitrogen cooled cryoshield. A mechanical shutter is
located in the first pumping stage, which enables control over beam introduction into the
main UHV chamber.

1.3.5 Plasma Characterization

The oxygen beam generated using the plasma source is comprised primarily of
molecular and atomic oxygen. Before investigating the surface chemistry of gas-phase
oxygen atoms, it is imperative to quantify the O-atom concentration in the beam. Several
plasma radical quantification tools including ultraviolet, visible, vibrational, and
ionization spectrosocopies have successfully been employed to quantify the radical density
in plasmas. The ultrahigh vacuum chamber, constructed for these studies, is equipped
with a mass spectrometer, allowing the use of mass spectrometric techniques to quantify
the O-atom beam concentration.
The first method used to detect the presence of O-atom radicals in the beam was line-of-sight threshold ionization mass spectrometry otherwise known as appearance potential spectroscopy, as discussed by Agarwal et al. [58]. This technique is based on the following principle. Electron impact ionization of oxygen atoms and molecules can yield the same ion. Consider generating O$^+$ ions for detection with the mass spectrometer. They can be generated by either direct ionization of O-atoms or through O$_2$ dissociation, as depicted by reaction Equations 1-1 and 1-2.

$$O + e^- \rightarrow O^+ + 2e^- \quad (E_1 = 13.8 \text{ eV}) \quad (1-1)$$

$$O_2 + e^- \rightarrow O^+ + O + 2e^- \quad (E_2 = 18.0 \text{ eV}) \quad (1-2)$$

The parameters $E_1$ and $E_2$ denote the threshold electron energies to generate O$^+$ ions through the processes shown in Equations 1-1 and 1-2 respectively, and are taken from reference 58. The direct ionization process (1-1) always has a lower threshold than the dissociative process (1-2) due to the additional energy required to break a molecular bond. This difference provides a means of detecting oxygen radicals in the plasma beam by monitoring the 16 amu signal intensity as a function of electron energy. Figure 1-8 shows appearance potential measurements taken with and without the plasma activated after a background subtraction taken at the lowest electron energy probed (12 eV). The beam with the plasma not activated shows the formation of O$^+$ ions before the threshold energy of 18.0 eV. This is attributed to thermal dissociation of O$_2$ on the hot filament in the ionizer, which is subsequently ionized and detected. Comparing the two traces shown, it may be seen that the O$^+$ ion signal at $E < 18$ eV increases by about an order of magnitude after activating the plasma. This increase provides direct evidence that O-atoms are present in the plasma-activated beam.
Alternatively, beam experiments may be performed to estimate the O-atom cracking fraction and at the same time search for contaminants. This allows the changes of the beam components to be quantified when activating or deactivating the plasma beam. This method is complicated in that introducing a beam into the chamber may also displace other gases from the chamber walls, which may be interpreted as beam components. The predominant components in the oxygen beam with the plasma not activated are 32 and 16 amu, with trace contaminants of 2 amu (hydrogen) and 28 amu (nitrogen). The measured 16 amu component arises from electron impact dissociation of O\textsubscript{2} in the mass spectrometer ionizer. The ion impact dissociation fraction was measured at a value of 10\%, which is close to the literature value of 12.3 \% for 70 eV electrons [59]. When the plasma was activated, the predominant component was still 32 amu, but an increase in the signals of masses 16, 18 and 30 amu was observed concurrent with a decrease in 28 and 32 amu. The rise in 16 amu is attributed to oxygen atom formation by the dissociation of O\textsubscript{2}, the rise in mass 18 is attributed to oxygen atom reactions with hydrogen to form water and plasma source outgassing, and mass 30 and is attributed to the conversion of nitrogen (mass 28) into NO (mass 30). The mass spectrometer sensitivity was increased to enhance the \textsuperscript{16}O atom signal, and masses 16, 18, 28 and 30 amu are shown in Figure 1-9 to compare the relative intensities of each beam component. At time equal to zero, the plasma has already been activated, and the shutter is closed. After 85 seconds, the shutter was opened and a rise in the mass 16 signal was observed. Two hundred seconds elapse and then the plasma is deactivated without changing the O\textsubscript{2} feed rate to the plasma discharge tube. The 16 amu signal was observed to drop. This
technique shows clearly the presence of oxygen radicals in the beam. Masses 18, 28, and 30 are shown in Figure 1-9 to illustrate the low contaminant levels in the beam.

The dissociation fraction may be estimated in the following manner. When the plasma is deactivated, it is reasonable to assume that the sole source of the m/e 16 signal is due to the dissociation of molecular oxygen in the ionizer. With an electron energy of 70 eV, this fraction is 10%, which provides a measure of the molecular oxygen flow rate with the plasma off. Since the pressure in the beam chamber remains constant when the plasma is deactivated, the beam flow rate is also assumed to remain constant. With this information, a mass balance can be performed on molecular and atomic oxygen and the dissociation fraction may be estimated using the following relationships.

\[
O_{2\text{tot}} = \frac{(P_{\text{off}} - P_0)}{0.10} \tag{1-3}
\]

\[
P_{\text{on}} - P_0 = \frac{2f(P_{\text{off}} - P_0)}{0.10} + (1 - f)(P_{\text{off}} - P_0) \tag{1-4}
\]

Here, \(P_{\text{on}}\), \(P_{\text{off}}\), \(P_0\), \(O_{2\text{tot}}\), and \(f\) are the \(^{16}\text{O}\) partial pressure when the plasma is on, the \(^{16}\text{O}\) partial pressure when the plasma is off, the baseline pressure, the total \(^{16}\text{O}_2\) entering the ionizer and the dissociation fraction, respectively. Equation 1-3 provides a measure of the total flow rate of \(O_2\) into the ionizer and the second expression may be solved to determine the dissociation fraction of O-atoms (f). Solving this expression for f yields an estimation of the \(O_2\) dissociation fraction of about 3% (flux of about 0.02 ML/sec). It should be noted that the flux of \(O_2\) into the ionizer consists of a background and a direct component. The background component can be measured by obstructing the beam flow path with the sample manipulator, preventing any direct \(O_2\) flux into the mass.
spectrometer. Once this value was obtained, it was subtracted off of the mass 16 partial pressure trace, providing a measure of the direct O$_2$ flux into the ionizer.

The final method used to determine the O-atom flux was to measure the oxygen uptake on Pt(111). Figure 1-10 shows the O-atom uptake curve as a function of exposure time while the sample was held at a constant temperature of 450 K. It is known that molecular oxygen will dissociatively adsorb onto the Pt(111) surface at this temperature and saturate at 0.25 ML. Therefore, any additional amount of oxygen deposited onto the surface is attributed to the adsorption of oxygen atoms. Within the first 180 seconds of the atomic oxygen exposure, the uptake curve is approximately linear. Assuming a unity sticking probability in this uptake region, the slope provides an approximation of the O-atom flux on the sample surface, which is 0.03 ML/sec. This is in reasonable agreement with the quantity determined by mass spectrometric methods especially considering that the sample is closer in proximity to the beam source than the mass spectrometer, yielding a higher atomic oxygen impingement rate onto the sample.

1.3.6 Gas Handling

A ¼ inch VCR manifold is used to direct the gases to various ports on the system. To minimize the introduction of contaminants in the gas, the manifold is evacuated with a 70 l/s turbo pump. The pressure inside the manifold is monitored using a thermocouple gauge tube. Gas lines from the manifold are connected to gas cylinders and all gas entry ports into the chamber.

1.3.7 Calibrated Molecular Beam

A typical means of exposing a sample to a gas in vacuum is to fill backfill the chamber with a gas for a measured period of time. The product of the pressure and the time provides a measure of the gas exposure on the surface. For example, an exposure of
about one monolayer of gas onto the surface corresponds to about one Langmuir, which is $10^{-6}$ Torr*sec. This poses a problem when gas dosing with “sticky” molecules such as water or ammonia, which could lead to long pump out times. Molecular beams provide a solution to this problem by providing an enhanced exposure to the sample surface while minimizing the gas load on the system. Several advantages are afforded by employing a calibrated molecular beam. If the gas flow rate is known, it becomes possible to directly measure gas uptake onto the surface and the sticking probability of the gas with coverage.

The beam operates under the following principles and is depicted by Figure 1-11. An example background partial pressure trace is shown in Figure 1-12. A mass balance on the gas-phase beam species is shown in Equation 1-5.

$$\frac{dN_g}{dt} = \dot{N} - \dot{N}_{out} - R_{ad}^{net}$$  \hspace{1cm} (1-5)

The quantities $N_g$, $R_{ad}^{net}$, $\dot{N}$ and $\dot{N}_{out}$ are the number of gas molecules in the system, the net adsorption rate, the total molecular flow rate into the system and the total molecular flow rate out of the system, respectively.

For large $S_p'$,

$$\frac{dN_g}{dt} \approx 0$$ \hspace{1cm} (1-6)

Equation 1-6 will be justified later. Substituting $PS_p'$ for $\dot{N}_{out}$ and rearranging Equation 1-6 yields:

$$P(t) = \frac{1}{S_p'} [\dot{N} - R_{ad}^{net}(t)]$$ \hspace{1cm} (1-7)

And
\[ R_{ad}^{\text{net}} = F\tilde{\Sigma}(\theta) - R_d(\theta) \]  

(1-8)

where \( \theta \) is the relative adsorbate coverage, \( S(\theta) \) is the sticking probability as a function of coverage, \( F \) is the intercepted fraction, and \( R_d(\theta) \) is the desorption rate from the surface.

If the exposure is conducted below the desorption temperature of the adsorbate, \( R_d(\theta) \) can be neglected. Substituting Equation 1-8 into 1-7 yields

\[
P(t) = \frac{\tilde{N}}{S_p} [1 - FS(\theta)]
\]

(1-9)

At \( t = \infty \), \( R_{ad}^{\text{net}} = 0 \), then \( P_\infty = \frac{\tilde{N}}{S_p} \) and \( P(t) = [1-P_\infty FS(\theta)] \), where \( P_\infty \) and \( P(t) \) are the steady state pressure after adsorption has ceased and the partial pressure as a function of time. Substituting this information into Equation 1-9 and rearranging yields the following expression:

\[
R_{ad}^{\text{net}} = \left[P_\infty - P(t)\right]S_p
\]

(1-10)

\[
\theta = \frac{\int_0^t R_{ad}^{\text{net}} d\tau}{\int_0^\infty R_{ad}^{\text{net}} d\tau}
\]

(1-11)

Winkler et al. performed calculations to determine the intercepted fraction \( F \) as a function of doser-sample distances and geometries [60], which allows \( F \) to be read directly from a chart provided in the reference. This derivation shows that adsorption rates and sticking probabilities can be determined directly from the background gas partial pressure traces. The relative coverage \( \theta \) can be determined by Equation 1-11. The next portion of this derivation will justify the approximation given by Equation 1-6.
Assuming the sample is already saturated with the gas, and no adsorption on a sample is occurring, Equation 1-5 can be written as Equation 1-12.

\[
\frac{dN_g}{dt} = \tilde{N} \cdot PS_p' \tag{1-12}
\]

Substitute \(N_g=PV/RT\) and \(S_p' = S_p/RT\), where \(S_p\) is the pumping speed in L/sec, \(R\) is the gas constant, \(V\) is the chamber volume in L, and \(P\) is the pressure in Torr.

\[
\frac{dP}{dt} = \frac{\tilde{N}RT}{V} - P \left(\frac{S_p}{V}\right) \tag{1-13}
\]

Let \(\tau_p\) equal the pumping time constant, where \(\tau_p = V/S_p\). For our system with only the turbo pump evacuating the chamber,

\[
\tau_p \approx \frac{50L}{200L/\text{sec}} = 0.25 \text{ sec} \tag{1-14}
\]

Equation 1-13 is a first order differential equation, when solved yields Equation 1-15.

\[
P(t) = P_\infty - e^{-t/\tau_p} (P_\infty - P_0) \tag{1-15}
\]

With such a small \(\tau_p\), the system pressure will reach \(P_\infty\) with shorter time scales than adsorption or reaction.

Figure 1-13 shows a schematic of the beam doser that has been mounted to the vacuum chamber via a single-axis translator. The calibrated molecular beam doser was assembled in the following manner. The primary components required for the beam doser were machined by the A&N Corporation, and consist of a ¼ inch stainless steel tube passing through a CF 275 blank flange and a head piece that mates with the tube through a VCR connection. A 10 micron diameter ¼ inch VCR gasket was obtained from Lenox Laser, and is used as the flow orifice. A glass micro-capillary array was obtained from Buhrl electro-optics and was mounted in the doser head to provide a
directed flux to the sample. The array is held place by a stainless steel cap. Outside of
the vacuum chamber, a 4-way CF 275 cross is used as the gas reservoir. Mounted to the
cross is a Baratron gauge capable of reading pressures from 0.01 to 10 Torr, inlet and
evacuation valves, and a line running up to the molecular beam doser. The flow rate
through the beam was controlled by regulating the pressure in the cross. To calibrate the
beam flow, the conductance across the pin hole was determined by the following
procedure. First the volume of the cross and all lines leading up to the gasket was
measured (255 ml). The cross was then charged with a gas to an initial pressure P_0. The
gas was allowed to flow out of the reservoir and through the pin-hole, while recording the
pressure inside the cross for an excess of 10 hours. By performing a mass balance of the
gas inside the cross, the pump out time constant was related to the conductance of the
orifice and the volume of the cross, in the following way.

The gas flow rate through an orifice of a known conductance is given by the
following expression,

\[
\frac{dP_1}{dt} = C(P_1 - P_2)
\]  

where C is the conductance, and P_1 and P_2 correspond to the pressure in the reservoir and
in the vacuum chamber, respectively. Since the pressure in the vacuum chamber is on the
order of \(10^{-10}\) Torr, P_2 can be neglected. The conductance of the pin hole may be
calibrated by measuring the pressure of the reservoir as time progresses. The pump out
rate follows the expression shown in Equation 1-17. Upon integration it yields an
exponential decay shown in Equation 1-18. A plot of the pressure decay in the reservoir
as a function of time is shown in Figure 1-14 and yields a time constant of 31758
seconds. In this example, the conductance is $8.03 \times 10^{-6}$ L/sec using carbon monoxide as the beam gas.

$$-V \frac{dp}{dt} = Cp$$  \hspace{1cm} (1-17)

$$p = p_0 e^{-ct/V}$$  \hspace{1cm} (1-18)

### 1.3.8 Calibration of O₂ Beam Flow from Plasma Source

The addition of the calibrated molecular beam to the system also provided the means for calibrating the flow rate of molecular oxygen through the plasma beam. Initiating the beam caused a rise in the pressure in the first stage of the beam chamber. Correlating the pressure rise in the first chamber with the oxygen flow rate provides a simple means of checking the beam flow rate. Using the mass spectrometer, the partial pressure of O₂ can be correlated with the beam chamber pressure. The pressure curve is then converted to number flow by comparing the measurements with those obtained by the calibrated molecular beam. A calibration curve is then obtained and is shown in Figure 1-15.

### 1.4 Detection Techniques

#### 1.4.1 Reaction Product Monitoring

In surface adsorption and chemical reaction systems, real time reaction kinetic data can be obtained by monitoring the temporal evolution of the background partial pressures of both reactants and products during the reaction. For a given experiment, a sample is prepared and exposed to a reactant beam. A derivation is given to illustrate the relationship of the monitored partial pressures to the reaction rate and is similar to the derivation shown in Section 1.3.7. For example, consider the dynamic displacement of
\(^{18}\text{O}_2\) from Pt(111) due to the impingement of \(^{16}\text{O}\)-atoms as shown in Figure 1-16. In this experiment, the surface was initially covered with 0.44 ML of \(^{18}\text{O}_2\) and then subsequently translated into the plasma beam path, while the shutter was closed. At time zero, the shutter was opened. The partial pressure of \(^{18}\text{O}_2\) initially jumped, and went through a maximum and then decayed to the baseline.

First, assume that the system is initially at steady state \((t < 0\ \text{sec.})\), with a constant background of 36 amu. This background is attributed to a constant leak rate of \(^{18}\text{O}_2\) and described by Equation 1-19,

\[
L = KS_p P_{eq}
\]  

(1-19)

where \(L\) is the leak rate, \(K\) is the conversion constant to molecular flow, \(S_p\) is the pumping speed in L/sec, and \(P_{eq}\) is the equilibrium pressure in Torr. The product \(K*S_p*P_{eq}\) is the rate at which gas is pumped out of the system. The leak rate could originate from species displaced from the walls or from the beam. Assume also that the gas desorbing from the surface does not re-adsorb during the course of the experiment. This is reasonable under the conditions examined in this study. A mass balance around the desorbing species is shown in Equation 1-20.

\[
A\tilde{N}(t) + L = KS_P + KV \frac{dp}{dt}
\]  

(1-20)

Here, \(A\) is the sample area, \(V\) is the volume of the chamber, and \(\tilde{N}\) is the desorption rate. Since the flux of the reagents remains constant during the experiment, the desorption rate can either be calculated as a function of reactant fluence or time. The second term on the right hand side of Equation 1-20 depicts the particle accumulation in the system due to a rise in the partial pressure. Combining Equations 1-19 and 1-20 yields the following expression.
\[ A\dot{N}(t) + KSP_{eq} = KSP + KV \frac{dp}{dt} \]  

(1-21)

Substitute \( a = A/KV, P^* = P - P_{eq}, \tau = V/S \), where \( \tau \) is the characteristic pump out time constant.

\[ a\dot{N}(t) = P^* + \tau \frac{dP^*}{dt} \]  

(1-22)

In Section 1.3.7, I showed that the derivative term could be neglected, leaving the desorption rate directly proportional to the partial pressure traces obtained from the mass spectrometer.

The area under the curve shown in Figure 1-16 is then directly proportional to the desorption yield of \(^{18}\text{O}_2\). If the desorption yield is known, the data shown in Figure 1-16 can be directly converted to the desorption rate in ML/s using the following expression, where \( s \) is a dummy integration variable, \( \Delta P \) is the pressure of the system minus the baseline, and \( \theta_0 \) is the initial coverage.

\[ rate = \theta_0 \frac{\Delta P(t)}{\int_0^\infty \Delta P(s) ds} \]  

(1-23)

### 1.4.2 Temperature Programmed Desorption and Reaction

Temperature programmed desorption and reaction techniques were used to quantify the amount of each species residing on the surface. These spectra also contain information regarding the desorption activation energy for each species [61,62]. The derivation relating the partial pressure to the desorption rate, shown in 1.3.7, also pertains to TPD analysis. Figure 1-17 shows an example TPD spectrum of atomic oxygen recombining on Pt(111) and desorbing as \( \text{O}_2 \) with \( \theta_0 \) equal to 0.25, 0.38, and 0.59 ML. Integrating the signal intensity of each spectrum gives the total amount of products
desorbing. Desorption features are observed at 550, 640, and 710 K. Each of these features is attributed to oxygen atoms residing in environments with different surface-adsorbate binding strengths. In this particular example, one can see the lower temperature desorption features increasing with $\theta_O$, indicating that the oxygen atoms are experiencing strong lateral repulsions from the neighboring atoms and have a weaker oxygen atom-surface bond.

1.4.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is a technique which entails illuminating the sample with X-ray radiation, and examining the energy of the photoelectrons evolving from the surface. The kinetic energy of these electrons is given by the terms of the Equation 1-24,

$$KE = h\nu - BE - \phi$$

where $h\nu$ is the photon energy, $BE$ is the binding energy of the electron, and $\phi$ is the work function difference between the sample and the electron analyzer. Each element has a unique electronic structure, and hence has its own unique XPS spectrum. The binding energy is a function of the local element bonding environment, giving this technique the means to probe the chemical state of each element. The photo-electrons are generated in the near surface region of the sample. The depth probed with this technique is characterized by the following expression,

$$d = \lambda \cos(\theta)$$

where $d$, $\lambda$, and $\theta$ represents the distance from the surface, electron mean free path, and the electron take off angle respectively. By varying the angle at which the photo-
electrons are taken, XPS will probe the concentrations of each species at different depths within the surface. This forms the basis for angle-resolved XPS.

Figure 1-1. Mechanisms describing surface chemical reactions. Left) The LH mechanism. Middle) The ER mechanism. Right) The HA mechanism.

Figure 1-2. UHV system constructed for our study.
Figure 1-3. Top view of the UHV system. A) Upper level. B) Lower level.
Figure 1-4. Specimen mount on the sample manipulator.
Figure 1-5. Sample temperature control scheme used for these experiments. Current is driven across the sample by the DC power supply, which is regulated by the controller.
Figure 1-6. Typical linear temperature ramp with a heating rate of 1 K/sec.
Figure 1-7. Beam chamber housing the plasma source. A) A cross-sectional top view. B) A side view.
Figure 1-8. Appearance potential measurement, monitoring O\(^+\) (m/e 16) with the plasma activated and deactivated with a first stage beam chamber pressure of 3.0\(\times\)10\(^{-5}\) Torr.
Figure 1-9. Mass spectrometer beam trace experiment taken with the plasma initially activated and the shutter closed with an electron energy of 70 eV. Masses 16, 18, 28 and 30 were monitored. After 85 seconds, the shutter was opened. Once 200 seconds have elapsed, the plasma was powered down, while maintaining the same O₂ flow rate.
Figure 1-10. Oxygen uptake on Pt(111) with a surface temperature of 450 K. The oxygen uptake is approximately linear in the range of 0-180 seconds, with a slope of 0.03 ML/sec.
Figure 1-11. Gas flow from the beam onto the sample, where \( \tilde{N} \), \( F \), and \( \tilde{N}_{out} \) represent the total molecular flow rate into the chamber (#/sec), the intercepted fraction by the sample and the total molecular flow rate out of the system. The system pressure (Torr) and the pumping speed (#/sec\(^{-1}\)(Torr\(^{-1}\)) are denoted as \( P \) and \( S_p ' \), respectively.
Figure 1-12. Hypothetical beam trace depicting the partial pressure of a gas using a calibrated molecular beam, where A is proportional to the quantity of gas adsorbed on the sample.
Figure 1-13. Molecular beam doser used for our experiments. A) Overall beam doser view. B) Beam doser head piece.
Figure 1-14. Pressure of carbon monoxide in the gas reservoir plotted as a function of time while pumping out through the laser drilled VCR Gasket. The first order decay time constant is 31758 seconds.
Figure 1-15. Calibration of the molecular oxygen flow rate through the beam chamber is compared with the pressure in the first differential pumping stage.
Figure 1-16. Dynamic displacement of $^{18}$O$_2$ taken upon exposing a Pt(111) surface saturated with $^{18}$O$_2$ to $^{16}$O-atoms, while holding the sample temperature constant at 90 K.
Figure 1-17. Temperature programmed desorption performed on Pt(111) after exposing to a beam of oxygen atoms. The surface coverage of oxygen atoms from lowest to highest coverage is 0.25, 0.38 and 0.59 ML.
CHAPTER 2
OXIDATION OF NITRIDE Si(100) BY GASEOUS ATOMIC AND MOLECULAR OXYGEN

The nitridation of Si(100) by ammonia and the subsequent oxidation of the nitrided surface by both gaseous atomic and molecular oxygen was investigated under ultrahigh vacuum (UHV) conditions using X-ray photoelectron spectroscopy (XPS). Nitridation of Si(100) by the thermal decomposition of NH₃ results in the formation of a subsurface nitride and a decrease in the concentration of surface dangling bond sites. Based on changes in the N1s spectra obtained after NH₃ adsorption and decomposition, we estimate that the nitride resides about four to five layers below the vacuum-solid interface and that the concentration of surface dangling bonds after nitridation is only 59% of its value on Si(100)-(2x1).

Oxidation of the nitrided surface is found to produce an oxide phase that remains in the outer layers of the solid, and interacts only weakly with the underlying nitride for oxygen coverages up to 2.5 ML. Slight changes in the N1s spectra caused by oxidizing at 300 K are suggested to arise primarily from the introduction of strain within the nitride, and by the formation of a small amount of Si₂-N-O species at the nitride-oxide interface. The nitrogen bonding environment changes negligibly after oxidizing at 800 K, which is indicative of greater phase separation at elevated surface temperature. Nitridation is also found to significantly reduce the reactivity of the Si(100) surface toward both atomic and molecular oxygen. A comparison of the oxygen uptake on the clean and nitrided surfaces shows quantitatively that the decrease in dangling bond concentration is responsible for
the reduced activity of the nitrided surface toward oxidation, and therefore that dangling bonds are the initial adsorption site of both gaseous oxygen atoms and molecules. Increasing the surface temperature is found to promote the uptake of oxygen when O\textsubscript{2} is used as the oxidant, but brings about only a small enhancement in the uptake of gaseous O-atoms. The different effects of surface temperature on the uptake of O versus O\textsubscript{2} are interpreted in terms of the efficiency at which dangling bond pairs are regenerated on the surface. In particular, it is suggested that elevated surface temperatures promote subsurface oxygen migration and concomitant regeneration of empty surface dimers, which are required for O\textsubscript{2} activation. In contrast, the availability of single dangling bonds needed for the adsorption of a gaseous oxygen atom is suggested to be relatively unaffected by the surface temperature.

2.1 Introduction

Silicon nitride and oxynitride films have been extensively investigated in recent years due to the advantages afforded by incorporating these materials into the dielectric layers used in metal-oxide-semiconductor (MOS) devices. The addition of small amounts of nitrogen to the SiO\textsubscript{2}-Si interface is known to improve the structural quality of the interface, and results in lower leakage current across the gate of a MOS device as well as enhanced resistance to boron diffusion into the SiO\textsubscript{2} [1]. The low activity of silicon nitride toward oxidation has also proved beneficial to the growth of alternative gate oxides such as Ta\textsubscript{2}O\textsubscript{5} and ZrO\textsubscript{2} that have higher dielectric constants (k) than SiO\textsubscript{2}. Recent investigations have shown that the deposition of high k oxides directly onto silicon can result in the formation of an SiO\textsubscript{2} layer that dominates the capacitance of the gate stack [2-6]. Incorporation of nitrogen in the near-surface region of silicon alleviates this problem by inhibiting SiO\textsubscript{2} formation during the deposition of Ta\textsubscript{2}O\textsubscript{5}, thereby
enabling the benefits of the high k oxide film to be more fully realized [7,8,63]. Another important application of silicon nitride is as a protective coating on ceramic components such as bearings and turbine blades for which tolerance to high temperature, oxidizing environments is critical. Despite these important applications, however, the oxidation of silicon nitride films is not well understood at the molecular level. In this article, we discuss results of an ultrahigh vacuum (UHV) investigation of the oxidation of a silicon nitride film by both gaseous atomic and molecular oxygen in which we focused our efforts on elucidating the fundamental origin for the oxidation resistance of nitrided silicon.

Several early studies have characterized the oxidation of thick silicon nitride films under conditions of high oxidant pressure [64-67]. For example, Kuiper et al. investigated the oxidation of a thick silicon nitride film by exposure to O$_2$ and H$_2$O in an atmospheric furnace. They report that the rate of oxidation of the nitride film is two orders of magnitude lower than the oxidation rate of Si(100), and that the presence of hydrogen (H$_2$ and H$_2$O) was necessary to oxidize the surface under the conditions examined. They assert that hydrogen reacts with the nitride to form gaseous ammonia and elemental silicon and that the surface activity toward oxidation is enhanced as a result since elemental silicon is more easily oxidized than the nitride. Similar results have been reported in studies of the dry oxidation of silicon nitride films [64,65,67]. While these investigations have characterized the oxidation resistance of silicon nitride at high pressure, experiments conducted under more well-defined and controllable conditions are needed to determine the underlying cause for the oxidation resistance of silicon nitride films. Experiments of this type have been reported recently by Wallace et
al. [68]. In this work, the investigators thermally decomposed ammonia on Si(111) to generate silicon nitride films in UHV and then oxidized the nitrided surface with molecular oxygen without breaking vacuum. From *in situ* analysis of the surface using X-ray photoelectron spectroscopy (XPS), the authors observed negligible oxygen uptake at surface temperatures below 873 K, and only a small amount of uptake above 873 K. The slow oxygen uptake was suggested to arise from a decrease in the concentration of surface dangling bonds after nitridation, though this effect was not quantified.

Prior investigations of the nitridation of Si(100) by NH₃ provide important insights for understanding how nitridation alters the properties of the Si(100) surface. At room temperature, ammonia adsorbs dissociatively on Si(100)-(2x1) to produce an adsorbed hydrogen atom and an NH₂ moiety [69-72]. Heating the ammonia-saturated surface to about 700 K then leads to the decomposition of adsorbed NH₂ and the complete desorption of hydrogen. Early investigations of this system also showed that the nitrogen atoms occupy subsurface sites after the NH₂ groups decompose [72,73]. For example, Dresser et al. [72] observed significant attenuation of the N(KLL) AES peak after sample heating, but only observed small amounts of NH₃ desorption (< 10%). From these observations, Dresser et al. concluded that nitrogen migrates to the sub-surface region after the adsorbed NH₂ species thermally decompose on Si(100). Subsequent studies have confirmed that nitrogen migrates to the subsurface of Si(100) during nitridation at elevated temperature (> 600 K) [74-78]. For example, using high resolution photoemission, Peden et al. [74] obtained compelling evidence that silicon nitridation by NH₃ occurs by a mechanism in which nitrogen atoms diffuse into the subsurface region and leave a thin layer of elemental silicon adjacent to the vacuum-solid interface that
persists as the underlying nitride film thickens. Experiments using low energy electron diffraction (LEED) also reveal that annealing the ammonia-covered surface results in a decrease in the intensity of the fractional order diffraction spots, signifying that NH$_2$ decomposition and nitrogen penetration to the subsurface disrupts the long-range order of the surface [79,80]. Considering that nitrogen resides below the vacuum-solid interface, direct interactions between an oxidant molecule and nitrogen may be expected to have only a minor influence on the oxidation behavior of nitrided Si(100). A change in the structure of the surface, as indicated by LEED experiments, may therefore be the predominant cause for the change in the reactivity of the surface toward oxidation.

Although few UHV investigations of the oxidation of silicon nitride films have been reported, the oxidation of single crystal silicon surfaces has been studied extensively. Of particular relevance to the present work are detailed UHV studies by Engstrom et al. [48] on the oxidation Si(100) and Si(111) by both gaseous atomic and molecular oxygen. These and other results may also be found in a review of Si oxidation written by Engel [49]. Briefly, under UHV conditions the dissociative adsorption of O$_2$ on Si(100) results in an effective saturation coverage of only about 1 ML of oxygen atoms when the surface is held at 300 K during oxidation. The saturation coverage can be increased by oxidizing at elevated surface temperature, but the oxygen uptake is still rather limited. For example, the saturation oxygen coverage increases to 2 ML when Si(100) is exposed to O$_2$ at a surface temperature of 800 K. Not surprisingly, Engstrom et al. [48] found that gaseous oxygen atoms adsorb on Si(100) with much higher probability than does O$_2$, and that oxygen coverages greater than 10 ML can be obtained by oxidizing Si(100) held at 300 K using an atomic oxygen beam. In contrast to the
results obtained using $O_2$, the uptake of oxygen atoms was found to be insensitive to the surface temperature for oxygen coverages up to about 5 ML, which is indicative of non-activated adsorption and possibly direct insertion of gaseous O-atoms into surface Si-Si bonds.

In the present study, we used X-ray photoelectron spectroscopy (XPS) to investigate the nitridation of Si(100) by the thermal decomposition of ammonia as well as the oxidation of the resulting nitride film by both gaseous atomic and molecular oxygen. The key objectives of this study were to determine the surface properties responsible for the oxidation resistance of silicon nitride films, and to characterize the mechanisms for oxidation with these oxidants and the properties of oxidized nitride films. We find that surface dangling bonds play a critical role in the adsorption of both O-atoms and $O_2$ and provide quantitative evidence that a decrease in the surface dangling bond concentration is the primary cause for the decrease in oxygen uptake by Si(100) after nitridation.

2.2 Experimental Methods

All experiments were conducted in an ultrahigh vacuum chamber described in Section 1.3. Briefly, this apparatus was equipped with a variable energy electron source, dual anode X-ray source capable of generating Al and Mg Kα radiation, ion source, and a hemispherical charged particle analyzer, giving the system the capability of performing Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Surface structural measurements were performed using low energy electron diffraction (LEED) optics. A commercial microwave plasma source was employed to generate an oxygen atom beam. The atom source was mounted in a stainless steel reaction chamber with two stages of differential pumping. The communication between the plasma source
and the vacuum chamber was through a quartz tube with a diameter of 6 mm and a length of 60 mm. The oxygen feeding the plasma source was supplied by BOC gases with a purity of 99.999% without any further purification.

The Si(100) sample used in this study was taken from an arsenic-doped (0.005 ohm-cm) silicon wafer that was cut and polished to within ± 0.5° of the (100) plane. An approximately 2 x 1 cm rectangular section was cut from the wafer, and tightly fastened to the Ta plates that contact the cooling reservoir of the manipulator. Only tantalum parts were used to fasten the Si sample to the holder since the use of stainless steel parts was found to introduce small amounts of nickel into the sample. To measure the sample temperature, a K type thermocouple was spot-welded to a thin strip of Ta foil that was bent into a U-shape and clipped to the back of the Si(100) sample. The sample was cleaned by sputtering with 2 keV Ar⁺ ions followed by annealing for several minutes at 1000 K. The sample was considered to be clean when no contaminants could be detected with XPS, and a sharp (2x1) LEED pattern was observed.

Ammonia was dosed onto the sample as a beam generated with the calibrated doser. Typical NH₃ fluxes used in these experiments were ~5 x 10¹³ cm⁻² sec⁻¹, which is estimated from the known NH₃ flow rate from the doser and the angular emission characteristics of micro-capillary arrays [57]. Exposures of NH₃ are reported in units of ML, where 1 ML is defined as the surface atom density of 6.8 x 10¹⁴ cm⁻² of the Si(100)-(2x1) surface.

Pure O₂ beams were dosed onto the sample by flowing oxygen through the plasma source with the microwave power disabled. The size of the beam spot on the sample was about 9 mm in diameter. We typically employed an O₂ beam flux of 0.26 ML/sec, which
was determined using the spot size estimate and by comparing the O$_2$ pressure rise in the UHV chamber due to the beam with that resulting from a known flow rate of O$_2$ admitted through the calibrated beam doser.

Beams containing oxygen atoms were generated by activating the microwave plasma with O$_2$ flowing through the source. With an initial O$_2$ flux of 0.26 ML/sec, a measurable change in the 16 amu intensity was not observed by line-of-sight mass spectrometry when the plasma was activated. To estimate the O-atom flux, the oxygen uptake was measured on clean Si(100)-(2x1) held at 300 K as a function of exposure to oxygen beams with and without the microwave power enabled. From a comparison with a previous investigation of the adsorption of gaseous O and O$_2$ on Si(100) [48], we estimate that O-atom fluxes of ~0.001 ML/sec impinged on the sample surface for the beam conditions employed. Subsequent to these experiments, it was determined that the beam source was slightly misaligned with the collimating apertures which caused substantial O-atom recombination prior to the beam entering the UHV chamber.

Although the O-atom fluxes that we employed were relatively low, significant enhancements in the rate of oxidation were observed when the surfaces under study were oxidized at a given fluence by a plasma-activated beam versus a pure O$_2$ beam. All XPS spectra reported in this study were obtained using Al K$_\alpha$ X-rays ($h\nu = 1486.6$ eV) with the analyzer operating in a retarding mode at a pass energy of 27 eV. The electron takeoff angle was varied by rotating the sample with respect to the analyzer axis. An angular resolution of ± 5° is estimated from the geometry of the analyzer, and electron takeoff angles are specified with respect to the surface normal. Unless stated otherwise, the spectra presented here were obtained by measuring photoelectrons emitted at an angle
of 60° from the surface normal. Even at this glancing takeoff angle, the area of the sample from which photoelectrons were collected was smaller than the spot size of the oxygen beam, thus ensuring that the XPS measurements probed only the regions of the surface that were dosed with gases. The XPS spectra presented here were each processed using 21-point Savitzky-Golay smoothing, followed by background subtraction using the Shirley method [81]. Oxygen coverages were determined from the ratio of O1s to Si2p integrated intensities, and assuming that exposure of clean Si(100)-(2x1) at 300 K to O2 produces a saturation coverage of 1 ML [48,49]. For the low oxygen coverages investigated here, we found it unnecessary to account for O1s and Si2p signal attenuation due to inelastic photoelectron scattering since the oxygen atoms remain in the outer surface layers. Nitrogen coverages were computed by a similar procedure, but inelastic scattering corrections were necessary in this case, as described in Section 2.3.

2.3 Results

2.3.1 NH3 Decomposition on Si(100)

An ultrathin nitride film was grown on the Si(100) substrate prior to each oxygen exposure by thermally decomposing 160 ML of ammonia on the surface at 900 K. Several layers of nitrogen incorporate into the solid during this exposure since ammonia decomposition and hydrogen desorption are rapid at 900 K [71,78]. The Si2p and N1s spectra obtained from the Si surface after this treatment are shown in Figures 2-1 and 2-2. The Si2p spectrum exhibits a main component at 99.2 eV due to elemental Si, and a smaller feature centered at about 101.8 eV. The small Si2p feature appears at a binding energy that is less than that of Si3N4 [74,77,78,82-85], which suggests the presence of a sub-stoichiometric nitride. For films prepared under similar conditions, previous
investigations suggest that silicon is present in a Si₃≡N configuration in which each N atom is bonded with three silicon atoms. The N₁s spectrum obtained after nitridation exhibits a single peak centered at a binding energy of 397.4 eV, which is also consistent with previous reports [77,78,82,86].

Experiments were conducted to probe the interaction of NH₃ with the Si(100)-(2x1) surface so that the properties of the nitride film could be characterized in more detail. XPS spectra were first obtained after exposing clean Si(100) held at 300 K to a saturation dose of 160 ML of ammonia. This exposure produces a nominal coverage of 0.5 ML of adsorbed NH₂ groups, with the balance of the surface sites occupied by hydrogen atoms, and these species do not undergo further reaction at 300 K under UHV conditions [72,75]. The N₁s spectrum obtained after the 300 K exposure exhibits a single peak centered at a binding energy of 398.1 eV (Figure 2-3A), which is consistent with previous reports of the N₁s binding energy of adsorbed NH₂ on Si(100) [73]. The N₁s spectrum shown in Figure 2-3B was then obtained after annealing the amino-covered surface for 5 minutes at 900 K, which results in the complete desorption of hydrogen from the surface. It is noted that the spectrum did not change from that shown in Figure 2-3B when the sample was annealed for longer times. After annealing, the N₁s peak position is shifted to a binding energy of 397.5 eV, which is consistent with the formation of Si₃≡N species in the near-surface region. Annealing the amino-saturated surface also causes the N₁s to Si₂p intensity ratio to decrease to about 60% of its initial value. The magnitude of this decrease is in excellent agreement with that observed by Dresser et al. [72] after heating amino-saturated Si(100) to temperatures greater than about 700 K and examining the surface with AES. Dresser et al. estimated that less than 10% of the nitrogen desorbs
from the surface during heating, and therefore attributed the reduction in the N KLL peak intensity to nitrogen penetration into the sub-surface [72].

From the intensity changes in the N1s and Si2p spectra, we estimated the distance at which the nitrogen atoms reside below the surface after annealing the amino layer. For this calculation, nitrogen desorption is neglected and it is assumed that all of the nitrogen atoms initially present in the amino layer reside in a single layer below the surface after the sample is heated to 900 K. It is further assumed that the probability of generating an N1s photoelectron is the same for an adsorbed NH2 group as for the nitride. Under these assumptions, the attenuated N1s to Si2p intensity ratio of 60% can be approximated by \( \exp(-x/\lambda \cos \theta) \), where \( x \) is the distance of the nitrogen atoms beneath the surface, \( \lambda \) is the inelastic mean free path of an N1s photoelectron through elemental Si and \( \theta \) is the photoelectron takeoff angle measured from the surface normal. Assuming an inelastic mean free path of 22.3 Å [87], the 40% decrease in N1s peak intensity suggests that the nitrogen atoms diffuse 5.8 Å below the Si surface layer. Based on the spacing between the Si layers closest to the (100)-(2x1) surface, this calculation suggests that nitrogen atoms reside between the fourth and fifth layers after the amino-covered surface is annealed at 900 K. Considering the simplicity of the analysis, our estimate is in good agreement with recent electronic structure calculations which predict that a nitrogen atom has a energetic preference to be located between the third and fourth layers of Si(100)-(2x1) and to bond with three Si atoms in the third layer [76].

After annealing the initial amino layer, the surface was held at 300 K and again exposed to 160 ML of ammonia. As may be seen in Figure 2-3C, this exposure causes the N1s peak to grow in intensity and to shift toward higher binding energy, which
indicates the presence of adsorbed NH$_2$ groups. Similar observations have been made by Avouris, Bozso and Hamers [73], and indicate that annealing the amino layer partially restores the reactivity of the surface toward ammonia dissociation. According to quantum chemical calculations [88,89], the dissociation of ammonia on Si(100)-(2x1) involves the adsorption of NH$_3$ on a single atom of a surface dimer, followed by N-H bond cleavage and hydrogen transfer to the opposing silicon atom of the dimer. Considering this prediction, it may be concluded that nitrogen diffusion into the subsurface of Si(100) regenerates *pairs* of surface dangling bonds, and thereby partially reactivates the surface toward ammonia dissociation. Interestingly, however, the increase in the N1s to Si2p intensity ratio after saturating the annealed surface with amino groups is only 54% of that obtained after saturating clean Si(100) with amino groups (Figure 2-3A). This difference suggests that nitrogen incorporation into the sub-surface of Si(100) is accompanied by a structural rearrangement of the surface that reduces the density of dangling bond pairs by nearly a factor of two from its value on the clean surface. Indeed, in a prior study, LEED images taken after ammonia decomposition on Si(100) show a diffuse background that eclipses the fractional order spots [79,80], indicating that nitrogen incorporation does alter the structure of the surface. The total dangling bond coverage on the nitrided surface may be estimated as 0.59 ML when all of the surface dangling bonds are assumed to exist in pairs, and taking into account attenuation of the N1s signal from subsurface nitrogen due to inelastic electron scattering from the NH$_2$ adsorbed at the surface.

As stated above, the procedure we employed for growing a nitride film for subsequent oxidation studies was to expose the clean surface held at 900 K to 160 ML of
ammonia. The intensity of the N1s peak obtained after this procedure (Figure 2-2) is about three times greater than that obtained from the amino-saturated Si(100) surface. To estimate the thickness of the nitride film, we assume that a layered structure is formed and that each layer contains 0.5 ML of nitrogen atoms. Furthermore, based on our analysis of the amino-saturated surface before and after annealing, it is assumed that the nitride layer closest to the vacuum-solid interface resides four to five layers below the surface; this assumption is supported by the oxidation results discussed below. With these assumptions, and invoking a simple model to account for signal attenuation due to inelastic electron scattering, we estimate that a nitride film of 5 to 6 atomic layers in thickness is generated by the 160 ML ammonia exposure at 900 K. The findings from these experiments that have a key impact on the understanding of oxidation of the nitrided surface are 1) that the nitride films produced by ammonia decomposition on Si(100) reside in the sub-surface region and 2) that nitridation reduces the density of surface dangling bond sites.

2.3.2 Oxidation of Nitrided Si(100) at 300 K

Atomic versus molecular oxygen. Oxidation of the nitrided surface by both molecular and atomic oxygen was investigated at a surface temperature of 300 K. After nitridation the surface was exposed to the oxygen beam for 60 minutes, and the surface was then analyzed with XPS. A 60 min beam exposure corresponds to ~930 ML of O2 for the fluxes employed. Exposing the nitrided surface to the pure O2 beam for 60 minutes results in an oxygen coverage of 0.27 ML, which was found to be the limiting coverage for oxidation of the nitrided surface at 300 K by O2. The oxygen coverage increased to 1.2 ML when the nitrided surface was exposed to the same beam fluence but
with the plasma power enabled. This result shows that gas-phase oxygen atoms are significantly more reactive toward nitrided Si(100) than is O₂, particularly considering that only about 3 ML of oxygen atoms are estimated to have impinged on the surface during the 60 minute exposure. The O₁s feature obtained after oxidizing with the plasma-activated beam is very similar in shape and peak location to that obtained after oxidizing with O₂ at 300 K (not shown). The O₁s peak is shifted to a higher binding energy by 0.1 eV after oxidizing with the plasma-activated beam, compared with oxidation with pure O₂, but this shift is consistent with the higher oxygen coverage that is achieved with the atomic oxygen beam. It is well known that as the coverage of oxygen is increased, the oxygen atoms on the Si(100) surface experience changes in their bonding environment that alters the O₁s binding energy [48,49]. The similarities in the O₁s spectra indicate that gaseous oxygen atoms and molecules produce similar chemical states of oxygen on the nitrided surface, which suggests that after adsorption (or O₂ dissociation) the processes by which oxygen atoms incorporate into the nitrided surface are independent of the identity of the gaseous oxidant. It therefore follows that the enhanced uptake achieved with the plasma-activated beam is due to the higher adsorption probability of oxygen atoms compared with O₂ on the nitrided surface.

**Clean versus nitrided Si(100).** A comparison of the oxygen uptake on the clean and nitrided Si(100) surfaces reveals that nitridation significantly lowers the surface reactivity toward oxidation. For example, exposing the clean surface to 930 ML of O₂ at 300 K results in an oxygen coverage of about 1 ML, whereas a coverage of only 0.27 ML is reached on the nitrided surface by oxidizing under the same conditions. The difference in the reactivity of these surfaces toward gaseous oxygen atoms is less pronounced, but is
still quite significant. Specifically, an oxygen coverage of 1.2 ML is obtained by exposing the nitrided surface at 300 K to the plasma-activated beam for 60 minutes, whereas a coverage of 2.1 ML is obtained on the clean surface for the same exposure and surface temperature. Since the nitride film is shown to reside several layers below the vacuum-solid interface, the lower reactivity of the nitrided surface compared with the clean surface does not arise from a direct interaction between nitrogen and oxygen (vide infra) but is attributed to the lower concentration of dangling bonds on the nitrided surface.

**Chemical state changes induced by oxidation at 300 K.** Shown in Figures 2-4 to 2-6 are the Si2p, N1s and O1s spectra obtained from the nitrided surface after depositing 1.2 ML of atomic oxygen at a surface temperature of 300 K. Also shown are the Si2p and N1s spectra obtained from the nitrided surface before oxidation, and the O1s spectrum obtained after exposing clean Si(100)-(2x1) held at 300 K to a saturation dose of O2, which results in about 1 ML of atomic oxygen on the surface. Each spectrum has been normalized by its peak height to facilitate comparison. Among all these spectra, the most distinct change caused by oxidation is an increase in the intensity of a feature centered at about 102 eV in the Si2p spectrum, see Figure 2-4. This spectral change indicates an increase in the amount of Si atoms present in partially oxidized states as oxygen atoms are incorporated within the nitrided surface. As discussed below, this feature is assigned specifically to Si$^{2+}$ and Si$^{3+}$ species that are directly bonded to oxygen atoms in the outermost surface layers.

The N1s spectra obtained before and after oxidation at 300 K are shown in Figure 2-5. Oxidation causes small changes in the N1s feature, but the changes observed are
reproducible and distinct. In particular, after oxidation the center of the N1s peak is shifted to lower binding energy by about 0.2 eV, and a small feature appears at a binding energy of 399.2 eV. Previous studies have reported that Si$_2$=N-O structures give rise to an N1s feature at a binding energy of about 399 eV. The appearance of the high binding energy shoulder is therefore consistent with a small quantity of N-O bonds being formed upon oxidation at 300 K. The incorporation of both nitrogen and oxygen atoms in the near-surface region of Si(100) has been found in most cases to cause the N1s peak to shift to a higher binding energy (BE) relative to the N1s BE obtained from pure nitride surfaces [76,90,91]. A positive binding energy shift of the N1s peak may result from a core-hole screening effect that arises from the formation of a dielectric film near the vacuum-solid interface. However, such a screening effect should be negligible for the films we have investigated since no more than 2 ML of oxygen atoms are present at the outer surface. Positive BE shifts of the N1s feature have also been attributed to a second nearest neighbor (NN) interaction in which oxygen atoms withdraw charge from Si atoms that are directly bonded to nitrogen in the film [76,91]. The negative binding energy shift of the main N1s feature observed in the present study suggests that at 300 K the majority of oxygen atoms do not penetrate far enough below the vacuum-solid interface to occupy second NN positions with respect to the nitrogen atoms. The small shift of the N1s peak to lower binding energy could be caused by the introduction of strain at the nitride-Si interface when oxygen atoms are incorporated into the top surface layers. Since these spectra show that the majority of the N and O atoms in the film do not directly interact, the growth of the 102 eV feature in the Si2p spectrum following oxidation may be
attributed to the formation of Si$^{2+}$ and Si$^{3+}$ species that are directly bonded to oxygen atoms in the outermost surface layers.

The O1s spectra obtained after depositing 1 and 1.2 ML of oxygen on the clean and nitrided surfaces, respectively, at 300 K are shown in Figure 2-6. The O1s peak obtained from the nitrided surface after oxidation is similar in shape to that obtained from the pure oxide layer, but is shifted to higher binding energy by about 0.3 eV. This difference in binding energies indicates that oxygen atoms at a concentration of about 1 ML experience slightly different chemical environments when adsorbed on clean versus nitrided Si(100) at 300 K. Based on the small N1s feature observed at 399 eV, a small fraction of the oxygen atoms appear to be directly bonded with nitrogen atoms in the film. This bonding interaction could alter the O1s binding energy, and produce a shift from the binding energy obtained from the pure oxide film. In addition, the oxygen atoms near the vacuum-solid interface, which do not directly bond with nitrogen, may experience a different chemical environment than a similar quantity of oxygen atoms incorporated into the clean surface. Such an effect could arise if the structures in the near-surface layers of the solid differ for the clean and nitrided surfaces. This latter interpretation is consistent with the ammonia uptake experiments which show that nitridation lowers the surface dangling bond density, probably by inducing a structural change at the surface.

**Angle-resolved XPS data.** The chemical changes suggested by the XPS spectra provide the general picture that oxidation of the nitrided surface at 300 K results in nearly segregated oxide and nitride layers, with the oxide layer being closer to the vacuum-solid interface. To further examine this possibility, XPS spectra were obtained at different
photoelectron takeoff angles to vary the depth resolution of the measurements. Shown in Figure 2-7 are the O1s and N1s spectra collected at 0 and 60° takeoff angles with respect to the surface normal after adsorbing 1.2 ML of oxygen atoms on the nitrided surface at 300 K. In order to illustrate the variation in the O1s/N1s intensity ratio with average sampling depth, the spectra obtained at a given takeoff angle are scaled by the integrated intensity of the N1s spectrum measured at that angle. Qualitative differences in the spectra obtained at different collection angles are slight, suggesting that the chemical states of nitrogen and oxygen remain fairly uniform throughout the film. The slight broadening of the N1s feature toward high binding energy at glancing takeoff angle may arise from a small amount of N-O bonding at the nitride-oxide interface closest to the surface. The most distinct difference between these spectra is clearly the increase of approximately 15% in the O1s/N1s intensity ratio for the measurements performed at a 60° takeoff angle, i.e. the more surface sensitive configuration. This result confirms that the oxygen atoms reside closer to the outer surface of the solid than do the nitrogen atoms when as much as 1.2 ML of oxygen atoms are adsorbed on nitrided Si(100) at 300 K.

2.3.3 Oxidation of Nitrided Si(100) at 800 K

Atomic versus molecular oxygen. Oxidation of the nitrided surface by both atomic and molecular oxygen was also investigated at a surface temperature of 800 K to compare with the oxidation behavior observed at 300 K, and to therefore assess the influence of surface temperature on oxidation. Increasing the surface temperature from 300 to 800 K significantly enhances the reactivity of the nitrided surface toward O2. In particular, exposing the nitrided surface to 930 ML of pure O2 produces an atomic oxygen coverage of 0.85 ML when the surface is held at 800 K, which appears to be a
saturation coverage for these oxidation conditions. In contrast, only 0.27 ML of oxygen is deposited by exposing the nitrided surface to O\textsubscript{2} at 300 K. The enhancement in reactivity with increasing surface temperature is less pronounced when oxidizing with oxygen atoms. For example, exposing the nitrided surface to the plasma-activated beam for 60 minutes produces oxygen coverages of 1.2 and 1.5 ML when the surface is held at 300 and 800 K, respectively. This is only a 25% increase in oxygen uptake, which is much lower than the 215% increase that is brought about by increasing the surface temperature when O\textsubscript{2} is used as the oxidant. Despite the small enhancement in oxygen uptake with surface temperature, a higher oxygen coverage is still obtained by oxidizing with gaseous O-atoms at 800 K compared with O\textsubscript{2}.

Similarities in the O1s spectra (not shown) indicate that similar chemical states of oxygen are generated on the nitrided surface when oxidation is conducted using either gaseous oxygen atoms or molecules at a surface temperature of 800 K. Thus, after adsorption (or dissociation) the processes by which oxygen atoms incorporate into the solid again appear to be independent of the identity of the gaseous oxidant, at least for the low coverages considered. The O1s peak does shift to higher binding energy by about 0.2 eV as the oxygen coverage on the nitrided surface is increased from 0.85 to 1.5 ML. However, this is a small difference in binding energy, considering that the oxygen coverage is nearly doubled, so it may be concluded that the increase in oxygen coverage from 0.85 to 1.5 ML causes only minor alterations to the chemical bonding environment of oxygen atoms incorporated into the nitrided surface at 800 K.

**Clean versus nitrided Si(100).** Table 2-1 summarizes the oxygen coverages obtained by oxidizing the nitrided and clean surfaces at the conditions indicated.
Examination of the coverages given in the table shows that the influence of surface temperature on oxygen uptake is similar for the nitrided and clean Si(100) surfaces. For example, a 930 ML O₂ exposure to clean Si(100)-(2x1) generates oxygen coverages of 1.0 and 2.0 ML at surface temperatures of 300 and 800 K, respectively. These coverages are in good agreement with previous studies [48,49], and demonstrate that oxygen uptake by the clean surface is enhanced considerably by increasing the surface temperature when O₂ is used as the oxidant, which is similar to the behavior found for the nitrided surface. As also observed for the nitrided surface, increasing the surface temperature produces a smaller increase in oxygen uptake by the clean surface when oxidizing with gaseous oxygen atoms. Table 2-1 shows that oxygen coverages of 2.1 and 2.4 ML result after exposing the clean surface to the plasma-activated beam for 60 minutes with the surface temperature maintained at 300 and 800 K, respectively. In the work by Engstrom et al. [48], it was found that atomic oxygen adsorption on the clean Si(100) surface remains independent of the surface temperature up to oxygen coverages of 4 to 5 ML. Thus, the relative insensitivity to surface temperature that we observed when oxidizing with the plasma-activated beam is expected for the oxygen coverages examined (< 3 ML). We do observe a small enhancement in uptake from the plasma-activated beam with increasing surface temperature. However, since O₂ is by far the majority beam component, this small enhancement in uptake most likely reflects the influence of surface temperature on O₂ incorporation.

**Chemical state changes induced by oxidation at 800 K.** Figures 2-8 to 2-10 display the Si2p, N1s and O1s spectra obtained after oxidizing the nitrided surface with oxygen atoms at a surface temperature of 800 K, which produces an oxygen coverage of
1.5 ML. Figures 2-8 and 2-9 also show the Si2p and N1s spectra obtained from the nitrided surface before oxidation. Figure 2-10 contains an O1s spectrum after depositing 2.4 ML of oxygen onto the clean Si(100) surface. Each spectrum has been normalized to its respective peak height to augment the contrasting features. The most pronounced spectral change following oxidation at 800 K is an increase in the intensity of the high binding energy feature in the Si2p spectrum (Fig. 2-9) that is centered at about 102 eV and extends to about 104 eV. The appearance of this feature indicates that Si+n (n > 0) states are generated during oxidation of the nitrided surface. While similar results were obtained following oxidation at 300 K (Figure 2-5), the intensity of the high BE Si2p feature is clearly greater and the feature extends to higher BE when oxidation is conducted at 800 K versus 300 K. The formation of a higher concentration of Si+n species not only arises from the higher oxygen coverages that are obtained during high temperature oxidation, but also from temperature dependent changes in the oxidation process. For example, for nearly the same oxygen coverage, we find that oxidation at 800 K versus 300 K results in a greater amount of Si+2, Si+3 and Si+4 states. This observation is consistent with the oxidation behavior of clean Si(100)-(2x1) [49]. At 300 K, oxidation occurs more uniformly across the surface, with the average Si oxidation state increasing in proportion to the oxygen coverage. Increasing the surface temperature enhances surface atom mobility and results in the formation of more highly oxidized clusters at relatively low oxygen coverage. The incorporation of oxygen into oxidized areas of the surface likely alleviates strain in the surface layers during oxidation.

Shown in Figure 2-9 are the N1s spectra obtained before and after oxidizing the nitrided surface at 800 K to reach an oxygen coverage of 1.5 ML. After oxidation, the
N1s peak is slightly narrower and the peak maximum is shifted by only about 0.1 eV to lower binding energy. Since these spectral changes are slight, it may be concluded that the nitrogen bonding environment is altered negligibly during oxidation at 800 K, at least when the oxygen coverage is increased up to 1.5 ML. Furthermore, the BE shift is in the opposite direction to that observed when O and N atoms occupy second NN sites [76,90,91], which suggests that the oxygen and nitrogen atoms in the film remain segregated, even though oxidation at the elevated temperature enhances surface atom mobility, as clearly evidenced by the formation Si\(^{+3}\) and Si\(^{+4}\) oxidation states at low oxygen coverage (Fig. 2-8). Interestingly, the N1s BE shift is smaller than that observed after oxidation at 300 K and the small feature at 399.2 eV is not evident in the N1s spectrum. These observations suggest that segregation of the nitride and oxide phases occurs to a greater extent at elevated surface temperature, with immeasurable formation of Si\(_2\)=N-O structures. Since the growth of highly oxidized SiO\(_x\) clusters involves substantial surface restructuring, it is conceivable that oxidation at the elevated temperature enables the sub-surface nitride to adopt a more favorable structure in which nitrogen atoms experience a more uniform bonding environment. Such a change may explain the slight narrowing of the N1s peak observed after oxidation of the nitrided surface at 800 K.

The O1s spectra obtained after oxidizing the clean and nitrided Si(100) surfaces at 800 K to oxygen coverages of 2.4 and 1.5 ML are remarkably similar (Fig. 2-10). Indeed, the similarity between the O1s spectra indicates that the presence of a nitride in the sub-surface of Si(100) has a negligible influence on the chemical state(s) of oxygen that form during oxidation at 800 K. Thus, it appears that SiO\(_x\) regions with similar
properties grow on clean and nitrided Si(100) at 800 K, despite the structural differences of these surfaces. The similarity in the O1s spectra (Fig. 2-10) is also consistent with enhanced segregation of the oxide and nitride phases when oxidation is conducted at elevated surface temperature.

**Angle resolved XPS data.** Analysis of the XPS spectra obtained after oxidizing the nitrided surface at 800 K provides evidence that the oxidized and nitrided regions remain segregated. Angle-resolved XPS spectra provide additional support for this interpretation. Figure 2-11 shows the O1s and N1s spectra obtained at electron take-off angles of 0° and 60° with respect to the surface normal, after adsorbing 1.5 ML of oxygen on the nitrided surface at 800 K. To compare the O1s/N1s intensity ratio as a function of sampling depth, the spectra obtained at a given angle have been normalized with respect to the N1s intensity at that angle. Only minor qualitative changes in the spectra obtained at different take-off angles are observed. For example, the O1s peak obtained at a 60° take off angle is shifted by only 0.1 eV to lower binding energy relative to the O1s peak obtained at an emission angle of 0°. Differences between the N1s spectra obtained at these take-off angles are slight. Similar to the angle resolved data obtained after oxidizing at 300 K, the O1s/N1s ratio increases by about 10% when the collection angle is adjusted to the more surface sensitive configuration. This observation confirms that oxygen resides closer to the vacuum-solid interface than does the nitride region.

**2.4 Discussion**

The present results show that nitridation of Si(100) at elevated temperature reduces the concentration of surface dangling bonds by nearly a factor of two and that the reactivity of the surface toward both atomic and molecular oxygen decreases significantly. Since the XPS results also reveal that the majority of oxygen and nitrogen
atoms do not directly interact within the films studied, but remain in nearly segregated layers, the decrease in surface dangling bond concentration appears to be the primary cause for the diminished activity of the nitrided surface. Physically, this conclusion implies that both gaseous oxygen atoms and molecules adsorb predominantly, if not exclusively, at dangling bond sites or pairs on the surface, and that the uptake of oxygen by the nitrided surface is limited by the availability of such sites. That dangling bonds are the active sites for O\textsubscript{2} adsorption is not at all surprising. In fact, quantum chemical calculations predict that the lowest energy pathway for O\textsubscript{2} activation on Si(100)-(2x1) involves the formation of a peroxy species across a surface dimer [89].

It is perhaps more surprising that gaseous oxygen atoms have such a strong tendency to adsorb at dangling bond sites since this implies that insertion directly into Si-Si bonds occurs to a negligible extent. While it is possible that an O atom incident from the gas-phase must overcome an activation barrier to directly insert into a Si-Si bond, we consider this possibility to be unlikely since formation of a Si-O-Si linkage is exothermic by at least 6 eV. A propensity for oxygen atoms to adsorb at dangling bonds, rather than to directly insert into Si-Si bonds, may be explained if we assume that the majority of oxygen atoms in the beam exist in the ground $^3$P electronic state and then consider electron spin effects. Because the $^3$P state is a triplet, direct O-atom insertion into a Si-Si bond is spin-forbidden whereas adsorption at a dangling bond site is not. In this case, the rate at which O-atoms from the beam directly insert into Si-Si bonds would be limited by the rate of non-adiabatic curve crossing events that transform the electronic configuration of the incident oxygen atom to a state such as the singlet $^1$D state for which direct insertion is allowed. Such events are likely to be rare in a single gas-surface collision at
thermal impact energy. Thus, the observation of selective O-atom adsorption at surface
dangling bond sites suggests that the initial adsorption event tends to be electronically
adiabatic for the beam conditions employed.

A quantitative comparison of the uptake of oxygen by the clean and nitrided
Si(100) surfaces provides additional insight for understanding the role of dangling bonds
in the oxidation of these surfaces. The bottom row of Table 2-1 shows the oxygen
coverages obtained on the nitrided surface relative to that obtained on the clean surface
for various oxidizing conditions. As may be seen in the table, the oxygen coverages
obtained by exposing the nitrided surface to the atomic oxygen beam at surface
temperatures of 300 and 800 K are 57 and 62.5% lower than that obtained on the clean
surface. These values are remarkably close to the ratio of dangling bond concentrations
on the nitrided and clean surfaces (59%), and provide quantitative evidence that gaseous
O-atoms adsorb preferentially on surface dangling bonds on both surfaces. This
comparison is even more favorable when considering that the contribution of O₂ to the
uptake achieved during the plasma-activated beam exposure is more significant at a
surface temperature of 800 K. Interestingly, for oxidation with O₂, the maximum oxygen
coverage obtained on the nitrided surface at 300 K is only 27% of that obtained on the
clean surface (Table 2-1). This value is less than half of the ratio of dangling bond
concentrations on the nitrided versus clean surfaces. Assuming that an O₂ molecule does
dissociate across a single dimer on the clean Si(100)-(2x1) surface, as predicted by
electronic structure calculations [89], this comparison suggests that at least two dimers
are consumed when a single oxygen molecule dissociates and the oxygen atoms
incorporate into the nitrided surface at 300 K. While it is difficult to envision four
dangling bonds being required to activate one \( \text{O}_2 \) molecule, it is conceivable that dangling bond pairs could be arranged on the nitried surface in such a way that \( \text{O}_2 \) activation on one pair could render a neighboring pair unable to readily activate a second \( \text{O}_2 \) molecule. The uptake of oxygen on the nitried surface increases to 44% of that on the clean surface when oxidation is conducted at 800 K using \( \text{O}_2 \), which may indicate that fewer dangling bond pairs are consumed or are more efficiently regenerated on the nitried compared with the clean surface during oxidation at elevated temperature. Overall, these observations suggest that oxidation with gaseous oxygen atoms occurs by a similar mechanism on the clean and nitried surfaces, with the main difference being that fewer adsorption sites are available on the nitried surface. In contrast, the mechanism for \( \text{O}_2 \) dissociative chemisorption and oxygen incorporation appears to be more sensitive to structural differences between the nitried and clean surfaces.

Increasing the surface temperature enhances the uptake of \( \text{O}_2 \) on both the clean and nitried surfaces, but produces only a small increase in the uptake of gaseous O-atoms. High surface temperatures are thought to facilitate the oxidation of clean Si(100) by \( \text{O}_2 \) by promoting oxygen penetration into the subsurface layers \[49\]. Such penetration is likely to regenerate dangling bond sites at the surface that are needed to activate \( \text{O}_2 \) molecules, thereby restoring the surface activity toward \( \text{O}_2 \) dissociation. It is noted that a molecular beam study by Ferguson et al. \[92\] shows that the dissociation probability of \( \text{O}_2 \) on Si(100) is only weakly dependent on the surface temperature at low gas-temperatures. Thus, more facile regeneration of active surface sites is the more likely explanation for the enhancement in oxygen uptake with surface temperature than would be promotion of \( \text{O}_2 \) bond cleavage at higher surface temperature.
The relative insensitivity to surface temperature in the uptake of gaseous O-atoms was first observed by Engstrom et al. [48] and was quite reasonably interpreted by those authors as evidence that oxygen atoms incident from the gas-phase insert readily into Si-Si bonds. The uptake of gaseous O-atoms was found to increase with surface temperature only at oxygen coverages greater than about 4-5 ML, which corresponds to oxygen atoms inserted into all of the Si-Si bonds that are directly accessible from the gas-phase. However, the findings from the current study indicate that surface dangling bonds are the preferred adsorption site for a gaseous O-atom, and that direct insertion into a Si-Si bond occurs to a negligible extent. Considering this finding, it is difficult to understand why an increase in the surface temperature effects only a small enhancement in the uptake of gaseous oxygen atoms. In particular, if more effective regeneration of surface dangling bond sites is the primary reason that an increase in surface temperature enhances O$_2$ uptake, then it is reasonable to expect that the uptake of gaseous oxygen atoms would also be promoted by raising the surface temperature since O-atoms also adsorb selectively at dangling bond sites and more of these sites should be available at high surface temperature.

A recent computational investigation by Widjaja and Musgrave [89] may offer a plausible explanation for understanding the different effects of surface temperature in the oxidation of Si(100) with gaseous O atoms versus O$_2$. The top panel of Figure 2-12 shows a schematic of key structures and the associated energy changes that were predicted to occur by those authors when O$_2$ adsorbs and then dissociates on the Si(100)-(2x1) surface [89]. It is important to note that the molecular representations shown in Figures 2-12 and 2-13 are only intended to depict the steps in the proposed model, and do
not precisely illustrate the bond lengths and angles for these structures as predicted by density functional theory. Following adsorption, the O₂ molecule is predicted to span the dimer to form a peroxy-like species that then dissociates to produce an oxygen atom inserted across the dimer and a siloxy radical. The oxygen atom of the siloxy radical then inserts into a Si-Si backbond, resulting in the final structure shown in the top panel. Clearly, the formation of a second peroxy species on the final structure would be significantly hindered by the presence of the O-atom bridging the dimer. Thus, if the oxygen atoms in this final structure have limited mobility, then effectively only one O₂ molecule can dissociate for each dangling bond pair on the surface. Notice that this situation would result in an oxygen coverage of 1.0 ML on the Si(100)-(2x1) surface, and may help to explain the substantial reduction in oxygen uptake that occurs at 1.0 ML when the clean surface is exposed to O₂ at 300 K.

The bottom panel of Figure 2-12 illustrates elementary steps by which the bridging oxygen atom could migrate to a backbond site. These reactions have not been explored computationally as far as we know. The first step in the scheme shows the formation of a siloxy radical by cleavage of an Si-O bond of the bridging oxygen species, and the second step involves oxygen insertion into a Si-Si backbond. This migration process regenerates an empty dimer, and would thereby enable a second O₂ molecule to bind in the peroxy configuration. Although energy barriers for these steps have not been explicitly predicted, the results of Widjaja and Musgrave suggest that the first step, production of the siloxy radical, should have the larger energy barrier. This barrier may be comparable to the 1.38 eV barrier required for the reverse of the final reaction shown in the top panel of Figure 2-12. Considering the large energy barrier, the migration of the
bridging oxygen atom to a backbond site should be promoted significantly by raising the surface temperature. Thus, according to this mechanism, oxygen uptake by \( O_2 \) dissociation is enhanced at elevated surface temperature since the population of empty dimers increases with increasing surface temperature.

Shown in Figure 2-13 are pathways proposed for the incorporation of a gaseous oxygen atom into the Si(100) surface. Based on the present results, the O-atom is assumed to adsorb initially on a dangling bond site to form a siloxy radical. From this site, the oxygen atom can insert either across the surface dimer or into a Si-Si backbond to form the structures shown in the figure. The energy changes illustrated in this figure were also taken from the work of Widjaja and Musgrave, and show only slight differences in the energetics of these insertion pathways. Since an O-atom adsorbs at a single dangling bond site, and therefore does not have the strict steric requirements for adsorption as does \( O_2 \), we speculate that a second O-atom will adsorb with roughly equal probability on each of the one O-atom structures shown in Figure 2-13. Thus, according to this interpretation, an increase in surface temperature has only a minor influence on the uptake of gaseous oxygen atoms because enhanced oxygen migration to sub-surface sites does not significantly affect the availability of single dangling bond sites at the surface.

2.5 Conclusions

We have investigated the nitridation of Si(100) and the subsequent oxidation of this surface by both gaseous atomic and molecular oxygen under UHV conditions. Nitridation of Si(100) by the thermal decomposition of ammonia at 900 K results in the formation of a subsurface nitride and a decrease in the concentration of surface dangling bond sites. Based on changes in N1s spectra after NH\(_3\) adsorption and decomposition, we estimate that the nitride resides four to five layers below the vacuum-solid interface and
that the concentration of dangling bonds on the nitrided surface is about 0.59 ML or 59% of that on the clean surface. Oxidation of the nitrided surface at surface temperatures of 300 and 800 K produces an oxide phase that resides in the outer surface layers and remains largely segregated from the subsurface nitride for oxygen coverages up to about 2.5 ML. At a surface temperature of 300 K, the incorporation of about 1 ML of oxygen into the near surface layers alters the nitrogen bonding environment only slightly, most likely by introducing strain in the subsurface nitride, and the N1s spectra indicate that a small quantity of Si$_2$=N-O also forms. At 800 K, the nitride bonding environment changes negligibly for oxygen coverages as high as 2.5 ML, which is consistent with greater segregation of the nitride and oxide phases and enhanced structural relaxation in these phases. In addition, at a given oxygen coverage, the quantity of Si$^{3+}$ and Si$^{4+}$ states that are detected increases when oxidation is conducted with the surface held at 800 K versus 300 K, indicating a tendency for regions of high local oxygen concentration to form at elevated temperature.

The reactivity of Si(100) toward both atomic and molecular oxygen decreases significantly after nitridation of the subsurface region due to the decrease in surface dangling bond concentration that accompanies nitride growth. Quantitative support for this conclusion is given by the observation that, for the same exposure to gaseous oxygen atoms, the oxygen coverage obtained on the nitrided surface relative to that on clean Si(100) is within 5% of the ratio of dangling bond concentrations on these surfaces. This finding also provides strong evidence that gaseous O($^3$P) atoms adsorb initially at dangling bond sites on these surfaces, and that direct insertion into Si-Si bonds occurs to a negligible extent. An increase in surface temperature is found to significantly enhance
oxygen uptake by the nitrided surface when O₂ is used as the oxidant, but brings about only a slight increase in uptake when gaseous oxygen atoms are employed. It is proposed that an increase in surface temperature promotes oxygen migration to the subsurface, and thereby results in more effective regeneration of empty dimers. Since the activation of an O₂ molecule on the Si(100) surface has more stringent steric requirements than does O-atom adsorption, the facile penetration of oxygen to the subsurface at high temperature has a greater influence on the adsorption of O₂ than O.
Table 2-1. Oxygen coverages on clean and nitrided Si(100)

<table>
<thead>
<tr>
<th></th>
<th>Atomic Oxygen</th>
<th>Molecular Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 K</td>
<td>800 K</td>
</tr>
<tr>
<td>[O] (nitrided)(^a)</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>[O] (clean) (^a)</td>
<td>2.1</td>
<td>2.4</td>
</tr>
<tr>
<td>nitrided/clean</td>
<td>0.57</td>
<td>0.62</td>
</tr>
</tbody>
</table>

\(^a\) The oxygen coverages in these rows are given in units of ML, as defined in the text, and were obtained after exposing the surface to the oxidant beam for 60 minutes at the surface temperatures indicated. A 60 min exposure corresponds to an O\(_2\) fluence of 930 ML when the plasma power is disabled, and to \(~928\) ML O\(_2\) and \(~3\) ML O when the plasma is activated.

Figure 2-1. Si\(_2\)p spectrum obtained from a Si(100) surface after a 160 ML NH\(_3\) exposure at a surface temperature of 900 K.
Figure 2-2. N1s spectrum obtained from a Si(100) surface after a 160 ML NH₃ exposure at a surface temperature of 900 K.
Figure 2-3. N1s spectra obtained from Si(100). A) After a 160 ML NH$_3$ exposure at 300 K. B) A subsequent anneal to 900 K for 5 minutes. C) A 160 ML exposure at a surface temperature of 300 K to the surface generated in B. The relative integrated areas of each N 1s spectrum is shown in each panel.
Figure 2-4. Si2p spectra obtained after exposing clean Si(100) to 160 ML NH$_3$ at a surface temperature of 900 K (dashed line), and after depositing 1.2 ML of oxygen on the nitrided Si(100) surface held at 300 K using the plasma-activated beam (solid line).
Figure 2-5. N1s spectra obtained after exposing Si(100) to 160 ML NH₃ at a surface temperature of 900 K (dashed line), and after depositing 1.2 ML of oxygen on the nitrided Si(100) surface held at 300 K using the plasma-activated beam (solid line).
Figure 2-6. O1s spectra obtained after incorporating 1 ML of oxygen atoms on Si(100) at a surface temperature of 300 K (dashed line), and after depositing 1.2 ML of oxygen on the nitrided Si(100) surface held at 300 K using the plasma-activated beam (solid line).
Figure 2-7. N1s and O1s spectra obtained at electron collection angles of 0° (dashed line) and 60° (solid line) after depositing 1.2 ML of oxygen on nitrided Si(100) at a surface temperature of 300 K. The O1s and N1s peak heights have been normalized to the N1s peak height at the respective angle.
Figure 2-8. Si2p spectra obtained after exposing clean Si(100) to 160 ML NH$_3$ at a surface temperature of 900 K (dashed line), and after depositing 1.5 ML of oxygen on the nitrided Si(100) surface held at 800 K using the plasma-activated beam (solid line).
Figure 2-9. N1s spectra obtained after exposing Si(100) to 160 ML NH₃ at a surface temperature of 900 K (dashed line), and after depositing 1.5 ML of oxygen on the nitrided Si(100) surface held at 800 K using the plasma-activated beam (solid line).
Figure 2-10. O1s spectra obtained after incorporating 2.4 ML of oxygen atoms on Si(100) at a surface temperature of 800 K (dashed line), and after depositing 1.5 ML of oxygen on the nitrided Si(100) surface held at 800 K using the plasma-activated beam (solid line).
Figure 2-11. N1s and O1s spectra obtained at electron collection angles of 0° (dashed line) and 60° (solid line) after depositing 1.5 ML of oxygen on nitrided Si(100) at a surface temperature of 800 K. The O1s and N1s peak heights have been normalized to the N1s peak height at the respective angle.
Adsorption and Insertion

![Diagram showing the dissociation of O₂ and its incorporation into Si(100). The top panel shows the structures and energetics for the dissociative chemisorption of O₂ on Si(100) as predicted by DFT calculations [89].]

\[ \Delta E = -2.84 \text{ eV} \]

\[ E^* = 1.5 \text{ eV} \]

\[ -2.81 \text{ eV} \]

\[ -0.83 \text{ eV} \]

Incorporation and Site Regeneration

![Diagram showing the migration of oxygen to the subsurface and the regeneration of an empty dimer.]

Figure 2-12. Model for O₂ dissociation and incorporation into Si(100). The top panel shows the structures and energetics for the dissociative chemisorption of O₂ on Si(100) as predicted by DFT calculations [89]. The bottom panel shows possible elementary steps for oxygen migration to the subsurface that results in the regeneration of an empty dimer.
Figure 2-13. Model for O-atom adsorption and incorporation into Si(100). The energy changes, where indicated, were predicted using DFT calculations as reported in reference 89.
CHAPTER 3
DYNAMIC DISPLACEMENT AND DISSOCIATION OF O₂ ON Pt(111) BY ATOMIC OXYGEN

The role of surface temperature on the dynamic displacement of $^{18}$O₂ from Pt(111) stimulated by the adsorption of $^{16}$O atoms was investigated. The maximum displacement rate increased with surface temperature, while the desorption yield decreased with temperature. Heteronuclear product evolution ($^{18}$O$^{16}$O) from the surface was below the experimental detection limits (< 10% of the $^{18}$O₂ product evolution). The adsorption of $^{16}$O-atoms also induced the dissociation of pre-adsorbed $^{18}$O₂ molecules at low surface temperatures. The initial displacement rates with a $^{16}$O-atom flux of 0.005 ML/sec were 0.0024, 0.0025 and 0.0027 ML/sec at 90, 100 and 110 K, respectively. Dissociation of $^{18}$O₂ was found to only occur during the first 0.2 ML fluence of $^{16}$O-atoms at which the total atomic oxygen coverage was about 0.44 ML. Estimates for the initial dissociation rate for $^{18}$O₂ at 90, 100 and 110 K and with the same $^{16}$O-atom flux was estimated of 0.0015, 0.0020 and 0.0030 ML/sec, respectively.

3.1 Introduction

Molecular oxygen displacement from Pt(111) by incident oxygen, nitrogen, and hydrogen atoms at 80 K was first reported by Rettner and Lee [17]. By adsorbing $^{18}$O₂ onto Pt(111) and subsequently exposing this surface to a beam of $^{16}$O-atoms at 80 K, they observed $^{18}$O₂ displacement from the surface. When exposing this surface to $^{16}$O-atoms, they also observed the formation of $^{16}$O$^{18}$O products. The displacement phenomenon was found to be independent of the adsorbing species, indicating that the desorption is not
collisionally induced. Using time-of-flight mass spectrometry, Rettner and Lee observed that $^{18}$O$_2$ desorbed with a bimodal energy distribution. This indicates that desorption occurs through two distinct channels. The lower energy component is consistent with thermal desorption, whereas the high energy feature indicates that a fraction of the adsorption energy of the incoming $^{16}$O-atom is transferred into the $^{18}$O$_2$ stimulating desorption.

Similar experiments were performed by Wheeler et al. [16]. Using a supersonic $^{16}$O-atom beam directed towards a Pt(111) surface saturated with $^{18}$O$_2$ at 77 K, they investigated the role of translational kinetic energy and incident angle on the initial molecular oxygen displacement rate. They observed both $^{18}$O$_2$ and $^{18}$O$^{16}$O evolving from the surface, and report that the initial probability of forming the mixed isotope species is $\sim$16.5 % of the total O$_2$ ($^{18}$O$_2$ and $^{18}$O$^{16}$O) displacement probability. These investigations also found that the displacement probability of $^{18}$O$_2$ increased with the initial translational energy and decreased at glancing incident angles of the $^{16}$O-atom beam. The probability of forming the mixed isotope product appeared to weakly depend on the $^{16}$O-atom energy and incidence angle.

From Rettner and Lee’s work it seems apparent that both thermal and nonthermal mechanisms govern the displacement of $^{18}$O$_2$ during the $^{16}$O-atom adsorption on Pt(111). During the $^{16}$O-atom exposure, the surface concentration of $^{16}$O-atoms is increasing. It is known that the presence of adsorbed oxygen atoms weakens the O$_2$-Pt bond [12,16], which could be responsible for the observed thermal desorption of $^{18}$O$_2$. Dynamic displacement is not fully understood, so it is reasonable that varying the surface temperature would provide additional information into the dynamic displacement
In this study, real-time reaction product monitoring and subsequent temperature programmed desorption (TPD) measurements were employed to examine the role of surface temperature on $^{18}$O$_2$ dynamic displacement stimulated by gaseous $^{16}$O-atoms.

### 3.2 Experimental Methods

These experiments were conducted in a three-level UHV chamber described in Section 1.3, with a brief description provided here. This chamber is equipped to perform X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low energy ion scattering spectroscopy (LEISS), reaction product monitoring, and TPD. The first plane contains a dual Al and Mg anode X-ray source, a variable energy electron source, a variable energy ion source, and a hemispherical charged particle analyzer. The second plane includes a calibrated molecular beam doser and a leak valve controlled molecular beam doser. The final plane contains a quadrupole mass spectrometer, a microwave plasma source mounted in a beam chamber with two stages of differential pumping, and a LEED optics. A microwave plasma source was employed to decompose molecular oxygen using 2.45 GHz microwave radiation. The end of the plasma source cavity is capped by an alumina faceplate with 5 laser drilled 0.4 mm through holes, which collimated the atom beam. A pair of oppositely charged plates ($\pm$ 10 kV/cm) is located at either side of the beam to remove charged particles from the beam path. The beam flows from the first stage to the second through a 3 mm skimmer, spaced 15 mm from the alumina collimating plate. This second stage is pumped via a 66 l/s turbo molecular pump and a liquid nitrogen cooled titanium sublimation pump. Communication from the second stage to the UHV chamber occurs through a quartz tube with a diameter and length of 6 mm and 60 mm, respectively.
The sample was mounted to a custom-built, liquid nitrogen cooled manipulator fabricated by McAllister Technical services. It is capable of 360° rotation about the vertical axis, and movement in all three Cartesian coordinates. The sample is cooled through thermal contact with a liquid nitrogen reservoir. Sample heating was conducted resistively using a DC power supply and the temperature was regulated using a PID controller.

The oxygen atom flux from the beam was estimated through measuring the $^{16}\text{O}$-atom uptake as a function of atom beam exposure. Assuming a sticking probability of unity, the flux was estimated at 0.005 ML/sec. The molecular oxygen flow rate into the UHV chamber was determined by monitoring the $^{16}\text{O}_2$ partial pressure rise with the mass spectrometer. This partial pressure was then compared to that of a rise with a known flow rate generated by the calibrated molecular beam doser and was measured at 0.1 ML/sec.

### 3.3 Results

Before each experiment, the sample was exposed to 20 Langmuirs (L) of $^{18}\text{O}_2$ which was sufficient to reach the saturation coverage (0.44 ML of $^{18}\text{O}_2$) at 100 K. The sample was then heated or cooled to the desired temperature. Immediately after saturating the sample with $^{18}\text{O}_2$, the $^{16}\text{O}_2$ plasma was ignited with the beam shutter in the closed position. Since the shutter is located in the first stage of differential pumping, no $^{16}\text{O}$-atoms flowed into the chamber containing the sample. The mass spectrometer was then activated, with the instrument sensitivity set to maximize the 34 amu ($^{16}\text{O}^{18}\text{O}$) and 36 amu ($^{18}\text{O}_2$) signal intensities. At this sensitivity, the count rate for $^{16}\text{O}_2$ was above the toleration limits for the electron multiplier, so the 32 amu signal was not monitored.
during the beam exposures. Upon opening the shutter, the sample was exposed to a mixture of 0.1 ML/sec of $^{16}$O$_2$ and 0.005 ML/sec of $^{16}$O-atoms. Under this flux condition, it is assumed that the total O$_2$ coverage ($^{16}$O$_2$ and $^{18}$O$_2$) remains saturated, although the saturation O$_2$ coverage decreases during the course of the $^{16}$O-atom exposure.

Shown in Figure 3-1 is the desorption rate of $^{18}$O$_2$ measured as a function of time as an $^{16}$O-atom beam impinges on the Pt(111) surface initially pre-saturated with $^{18}$O$_2$ at surface temperatures $T_s$ of 90, 100 and 110 K. In each of the traces, the $^{18}$O$_2$ desorption rate increases abruptly when the beam exposure is initiated. After a short time delay of about 30 seconds, the desorption rate reaches a maximum, and then decays to the initial baseline, suggesting that all of the $^{18}$O$_2$ desorbed from the surface within 250 seconds or equivalently after only about 1.25 ML of $^{16}$O-atoms collided with the surface. In similar experiments, Wheeler et al. [16] also observed the $^{18}$O$_2$ desorption rate to pass through a maximum as an $^{16}$O-atom beam was directed toward an $^{18}$O$_2$-presaturated Pt(111) surface, and suggested that a decrease in the O$_2$-Pt binding strength as the $^{16}$O-atom coverage increases may cause the $^{18}$O$_2$ desorption rate to increase producing the rate maximum. In the present study, the time delay before the desorption rate maximum is also found to be independent of the surface temperature, but the value of the maximum desorption rate increases with temperature and the desorption rate decreases to the baseline after the maximum more quickly at higher surface temperatures.

The partial pressure of $^{18}$O$^{16}$O was also found to increase when the $^{16}$O-atom impinged on the $^{18}$O$_2$-covered surface, but the $^{18}$O$^{16}$O molecules do not appear to evolve from the Pt(111) surface. The $^{18}$O$^{16}$O partial pressure increased to about twice the level
as the initial $^{18}\text{O}_2$ desorption rate, but remained approximately constant during the beam exposure, even after the $^{18}\text{O}_2$ desorption rate had returned to its baseline value, and the $^{18}\text{O}^{16}\text{O}$ partial pressure dropped back to its initial level only after the flow of $^{16}\text{O}$-atoms into the chamber was terminated. The quantity of $^{18}\text{O}^{16}\text{O}$ in the beam did not change when the plasma was deactivated, indicating that the 34 amu signal is due to the natural abundance of $^{18}\text{O}^{16}\text{O}$ in the beam. Wheeler et al. [16] also observed an increase in the $^{18}\text{O}^{16}\text{O}$ partial pressure during their beam experiments. Recall that they observed an initial $^{18}\text{O}^{16}\text{O}$ formation rate of 16.5 % [16]. In the present study, an increase in the $^{18}\text{O}^{16}\text{O}$ partial pressure arising from such an exchange reaction is difficult to detect due to the relatively high 34 amu background intensity that was observed. The $^{18}\text{O}_2$ gas used in the present study consists of about 0.4% as measured by the mass spectrometer. With the high 34 amu background in these experiments, the $^{18}\text{O}^{16}\text{O}$ products were less than 10% of the $^{18}\text{O}_2$ displacement rate.

Another possibility is that the exchange reaction is more probable for the beam conditions employed by Wheeler et al. [16]. These authors generated supersonic beams by expanding mixtures of He/$^{18}\text{O}_2$ and Ar/$^{18}\text{O}_2$ from RF plasma operating pressures near 1 bar, and produced O-atoms with kinetic energies in the range of 0.20 to 0.47 eV. In the current study, gaseous O-atoms with kinetic energies of $\sim$0.05 eV were generated by flowing pure $\text{O}_2$ through a microwave plasma operating at about $10^{-2}$ Torr from which the flow is effusive. The differences in these plasma conditions could certainly affect the composition of the plasma, and hence the surface reactivity that is observed. Finally, $^{18}\text{O}_2$ and $^{18}\text{O}^{16}\text{O}$ were not observed to desorb at low $T_s$ when the $^{18}\text{O}_2$ covered surface
was exposed to the beam with the plasma-power disabled, which shows that the $^{18}\text{O}_2$ desorption is stimulated by the impingent $^{16}\text{O}$-atoms.

Integration of the $^{18}\text{O}_2$ desorption traces reveals that the total amount of $^{18}\text{O}_2$ that desorbs during the $^{16}\text{O}$-atom beam exposure decreases when the experiments are conducted at increasing surface temperatures. Specifically, the desorption yields at $T_s = 100$ and $110$ K are 9% and 20% lower, respectively, than the desorption yield measured at $90$ K. This result is surprising since the lack of measurable $^{18}\text{O}^{16}\text{O}$ evolution from the surface was initially believed to indicate that desorption is the only process by which the coverage of adsorbed $^{18}\text{O}_2$ molecules is depleted during the experiments. Moreover, the decay of the $^{18}\text{O}_2$ desorption rate back to its initial baseline value also suggests that all of the $^{18}\text{O}_2$ molecules desorb. Clearly, however, a significant fraction of the $^{18}\text{O}_2$ molecules initially adsorbed on the surface do not desorb as $^{16}\text{O}$-atoms impinge on the surface.

Since $^{18}\text{O}$ was only observed to desorb as $^{18}\text{O}_2$ during the $^{16}\text{O}$-atom beam exposure, the decrease in the $^{18}\text{O}_2$ desorption yield with increasing surface temperature suggests that $^{18}\text{O}$ remains on the surface at the end of the beam experiments. To examine this possibility, a temperature programmed desorption measurement was performed at the completion of each $^{16}\text{O}$-atom beam exposure to monitor for the evolution of $^{16}\text{O}_2$, $^{18}\text{O}^{16}\text{O}$ and $^{18}\text{O}_2$ from the surface. Indeed, as shown in Figure 3-2, each of these isotopomers was observed to desorb during TPD, confirming that $^{18}\text{O}$ remains on the surface after the dynamic displacement of $^{18}\text{O}_2$ by gaseous $^{16}\text{O}$-atoms is completed at low $T_s$. Notice that the TPD trace for each isotopomer is similar in shape, and that desorption occurs at high rates over a narrow range of temperature centered at about 620 K. The recombinative desorption of oxygen atoms gives rise to O$_2$ desorption at these high temperatures, while
desorption of molecularly adsorbed $O_2$ occurs at temperatures near 150 K. Thus, the TPD results indicate that the vast majority of $^{16}O$ and $^{18}O$ species are present in atomic form on the surface after the dynamic displacement experiments are complete, though a small quantity of molecularly adsorbed $^{16}O_2$ is also present on the surface, as indicated by the small desorption feature observed at low temperature in the TPD spectra. Integration of these TPD spectra reveals that ~1.4 ML of $^{16}O$ atoms adsorb on the surface during a 6 minute (1.80 ML $^{16}O$-atom fluence) beam exposure.

To determine if $^{18}O$ could exist on the surface in molecular form after the beam exposure, and then dissociated during TPD, we adsorbed about 1.4 ML of $^{16}O$-atoms on the initially clean Pt(111) surface and then attempted to saturate the surface with $^{18}O_2$ at 90 K. Subsequent TPD analysis revealed that only small quantities of $^{18}O_2$ (<0.03 ML) could be adsorbed on the surface at this high $^{16}O$-atom coverage, and that the $^{18}O_2$ that adsorbs does not dissociate during TPD. Hence, it may be concluded that only atomic $^{18}O$ remains on the surface after the $^{16}O$-atom beam exposure, and therefore that $^{18}O_2$ dissociates as $^{16}O$-atoms impinge upon the surface at $T_s < 110$ K. The similar shapes of the desorption traces indicate that the $^{16}O$ and $^{18}O$ species populate the same adsorption states, which is also consistent with each isotope being adsorbed in atomic form after $^{18}O_2$ dissociation is completed at low surface temperature. We recently investigated the oxidation of Pt(111) by gaseous O-atoms and found that Pt oxide forms on this surface at atomic oxygen coverages greater than about 0.75 ML. Thus, the lack of appreciable $O_2$ adsorption on Pt(111) covered by about 1.4 ML of O-atoms indicates that $O_2$ binds weakly on Pt oxide, which is consistent with recent findings for CO adsorption on this surface as discussed in Chapter 4.
A series of $^{18}\text{O}^{16}\text{O}$ TPD spectra obtained after completing the dynamic displacement experiments at surface temperatures of 90, 100, and 110 K are shown in the right panel of Figure 3-2. These spectra show an increase in the $^{18}\text{O}^{16}\text{O}$ desorption yield measured after $^{16}\text{O}$-atom beam exposures performed at increasing surface temperatures from 90 to 110 K. In fact, the amount of $^{18}\text{O}$ atoms residing on the surface, as determined from the post-exposure $^{18}\text{O}^{16}\text{O}$ and $^{18}\text{O}_2$ TPD spectra, is within 5% of the decrease in the $^{18}\text{O}_2$ desorption yield, determined by integrating the direct $^{18}\text{O}_2$ displacement traces (Fig. 3-1). The agreement between these analyses supports the interpretation that the concentration of adsorbed $^{18}\text{O}_2$ is reduced to zero during the $^{16}\text{O}$-atom beam exposure at low $T_s$ by only two reaction channels, namely, direct $^{18}\text{O}_2$ desorption and dissociation for which the resulting $^{18}\text{O}$ atoms remain on the surface.

The absolute $^{18}\text{O}_2$ dissociation yield as a function of the temperature of the surface during $^{16}\text{O}$-atom bombardment can also be determined from the integrated $^{18}\text{O}^{16}\text{O}$ and $^{18}\text{O}_2$ TPD spectra obtained after the beam experiments. To determine the $^{18}\text{O}$-atom coverages from this TPD data, the areas under the TPD traces were scaled by the $^{18}\text{O}_2$ TPD area obtained after thermally dissociating $^{18}\text{O}_2$ on Pt(111) until saturation, which is well known to result in an $^{18}\text{O}$-atom coverage of 0.25 ML. The displacement yield can then be determined by applying the mass balance shown in Equation 3-1, in which it is assumed that the pre-adsorbed $^{18}\text{O}_2$ is depleted from the surface only through direct displacement or dissociation; this assumption is in good agreement with the data analysis discussed above. As shown in Table 3-1, the amount of $^{18}\text{O}_2$ that dissociates as $^{16}\text{O}$-atoms impinge on the surface is quite sensitive to the surface temperature, increasing from 0.06 to 0.11 ML with a relatively small increase in the surface temperature from 90
to 110 K. Also, the dissociation yields at 90 and 110 K represent 13.6 and 25 % of the initial $^{18}\text{O}_2$ coverage, indicating that a significant fraction of the adsorbed molecules dissociate during the atomic oxygen beam exposure. Recall that the formation rate of the mixed isotope product was below the detection limits (~10%). The dissociation yields shown are greater than this quantity, indicating that the dissociation rates are greater than the exchange product formation rate under the conditions examined.

$$^{18}\text{O}_{2(\text{g})} = 0.44\text{ML} - Y^{(18}\text{O}_{2\text{dis}})$$  \hspace{1cm} (3-1)

The analysis discussed above predicts the total amount of $^{18}\text{O}_2$ molecules that dissociate during the 1.8 ML $^{16}\text{O}$-atom beam exposure to the surface, but it does not provide information about the variation of the dissociation yield with $^{16}\text{O}$-atom fluence. To determine how the dissociation yield changes with $^{16}\text{O}$-atom fluence, or more specifically, with the total atomic oxygen coverage, the $^{18}\text{O}_2$ saturated Pt(111) surface was exposed to $^{16}\text{O}$-atom beam for durations of 20, 40, 60, 80 and 200 seconds, which corresponds to $^{16}\text{O}$-atom fluences of 0.1, 0.2, 0.3, 0.4 and 1 ML, and TPD was performed after each exposure. The TPD spectra were then integrated to determine the amount of $^{18}\text{O}_2$ molecules that dissociate at different surface temperatures as a function of the $^{16}\text{O}$-atom exposure. Recall that chemisorbed $\text{O}_2$ thermally dissociates during TPD if the total atomic oxygen coverage is less than 0.25 ML. Therefore, this analysis can provide a measure of the coverage of $^{18}\text{O}$-atoms present on the surface only when the total O-atom coverage ($^{16}\text{O} + ^{18}\text{O}$) is greater than 0.25 ML, otherwise it is not possible to distinguish $^{18}\text{O}$ present in atomic form at $T_s < 110$ K from $^{18}\text{O}$ atoms generated by the thermal dissociation of $^{18}\text{O}_2$ during the TPD measurement. From this analysis, $^{18}\text{O}_2$ dissociation was found to occur only during the first 40 seconds (~0.2 ML $^{16}\text{O}$-atom fluence) of the
beam exposure, producing $^{18}$O atom coverages of 0.12 and 0.22 ML at surface
temperatures of 90 and 110 K, respectively. At $T_s = 110$ K, the $^{18}$O-atom coverage nearly
doubles, increasing from 0.14 to 0.22 ML, as the beam exposure continues from 20 to 40
seconds. Analysis of the TPD spectra also reveals that the total coverage of O-atoms
increases from 0.26 to 0.44 ML during the 20 to 40 second time interval over which $^{18}$O$_2$
molecules continue to dissociate efficiently. This is an interesting result since the thermal
dissociation of O$_2$ on Pt(111) under UHV conditions ceases once the total atomic oxygen
coverage reaches 0.25 ML. Thus, the observation of $^{18}$O$_2$ dissociation above this limiting
O-atom coverage, and at low surface temperature, supports the interpretation that the
dissociation is stimulated by interactions between the adsorbed O$_2$ molecules and the O-
atoms incident from the gas-phase.

Since the O$_2$-Pt(111) binding energy decreases as the atomic oxygen coverage
increases during the beam exposure, it is important to estimate the contribution of thermal
desorption to the total rate of $^{18}$O$_2$ desorption observed during the $^{16}$O-atom beam
exposures. Shutter interruption experiments were performed to determine how the
thermal desorption rate varies during the beam exposures. In these experiments, the
mechanical shutter was interposed in the beam path to abruptly discontinue $^{16}$O-atom
impingement onto the sample surface at different times, and hence atomic oxygen
coverages. Shown in Figure 3-3 are the $^{18}$O$_2$ desorption traces obtained at surface
temperatures of 90 and 110 K when the beam exposure was continued and discontinued
in 30 second intervals. At the start of the experiment, the surface is initially saturated
with only $^{18}$O$_2$ molecules. If the thermal desorption of $^{18}$O$_2$ is negligible, then the $^{18}$O$_2$
desorption rate should drop to its initial baseline value upon discontinuing the $^{16}$O-atom
beam exposure, and should return to the level observed before terminating the exposure when the shutter is opened again. At $T_s = 90$ K the $^{18}\text{O}_2$ partial pressure drops rapidly when the beam exposure is interrupted at 30 seconds and nearly returns to the initial baseline (Figure 3-3). Upon reopening the shutter, the desorption rate rose to a value nearly equal to that observed at the end of the first 30 second exposure. These changes show that the thermal desorption of $^{18}\text{O}_2$ occurs very slowly at 90 K as the O-atom coverage increases.

The thermal desorption of $^{18}\text{O}_2$ occurs at a measurable rate during the beam exposure at $T_s = 110$ K. Figure 3-3 shows that the $^{18}\text{O}_2$ desorption rate drops abruptly when the beam exposure is terminated at 30 seconds, but reaches a value well above the initial baseline, and then decays significantly during the 30 seconds that $^{16}\text{O}$-atom beam is isolated from the chamber. Specifically, the desorption rate observed immediately after terminating the beam exposure for the first time is about 24% of the maximum rate obtained during the first 30 second beam exposure, but after 30 seconds without exposing the sample to the beam, the desorption rate is only about 6% of the highest rate observed during the initial exposure period. The decay of $^{18}\text{O}_2$ thermal desorption rate indicates that the thermal desorption channel is slowly deactivating, despite the abundance of $^{18}\text{O}_2$ remaining on the surface. A likely interpretation is that $^{18}\text{O}_2$ residing in regions near the O-adatoms are desorbing. When the shutter is reopened at 60 seconds, the desorption rate jumped to a value that is lower than that observed at 30 seconds and then rises to a maximum and decreases, until the beam is re-interrupted. Upon reopening the shutter, the surface concentration of O-atoms begins to increase again. The observation of a new maximum indicates that thermal desorption component becomes reactivated as the O-
adatom coverage grows. These changes show that $^{18}$O$_2$ thermally desorbs at appreciable rates at $T_s = 110$ K as the coverage of O-atoms increases during the beam exposure, but that the thermal desorption rate is nearly negligible during the beam experiments at 90 K. Using the thermal desorption rates determined from the beam interruption experiments, it is estimated that about 0.04 ML and 0.004 ML of the $^{18}$O$_2$ thermally desorbs during the 6 minute beam exposures performed at $T_s = 90$ and 110 K, respectively. Thus, the thermal desorption of O$_2$ accounts for only a small fraction of the total amount of $^{18}$O$_2$ molecules that desorb while the $^{16}$O-atom beam impinges on the surface, at the temperatures examined.

3.4 Discussion

Dynamic displacement and dissociation of $^{18}$O$_2$ was observed to occur when directing a beam of $^{16}$O-atoms toward Pt(111) saturated with $^{18}$O$_2$ at temperatures between 90 and 110 K. Molecular oxygen dissociation at low surface temperatures have also been observed when exposing O$_2$-covered Pt(111) to gaseous hydrogen atoms [14] or an electron beam [9]. The experiments conducted here show that the probability for $^{18}$O$_2$ dissociation increases significantly with a modest change in the surface temperature. At $T_s = 110$ K, the adsorbed $^{18}$O$_2$ continues to dissociate under the $^{16}$O-atom flux when the total O-atom coverage, $\theta_O (\theta_{^{16}O} + \theta_{^{18}O})$, increases above 0.25 ML. The thermal dissociation of O$_2$ on Pt(111) ceases under UHV conditions once the O-atom coverage reaches 0.25 ML so the observation of $^{18}$O$_2$ dissociation above this coverage is convincing evidence for a dissociation mechanism in which a substantial amount of the $^{16}$O adsorption energy is transferred to the $^{18}$O$_2$ molecules, efficiently stimulating desorption or dissociation. The dissociation of $^{18}$O$_2$ occurred only during the first 40
seconds (0.2 ML O-atom exposure) of the beam experiment at each surface temperature, indicating that the dissociation probability depends on the total O-atom coverage, and decreases to zero once a critical $\theta_O$ is reached. This observation is consistent with reports that the energy barrier for O$_2$ dissociation on Pt(111) increases significantly with increasing O-atom coverage [51].

To gain insights for understanding the surface temperature dependence of the O$_2$ dissociation probability induced by incident O-atoms, it is useful to consider the behavior of O$_2$ on Pt(111) in the absence of impinging oxygen atoms. Molecular oxygen chemisorbs associatively on Pt(111) at 100 K. Two distinct types of adsorbed O$_2$ species have been identified on Pt(111) using high resolution electron energy loss spectroscopy, ultraviolet photoemission spectroscopy and near-edge X-ray absorption spectroscopy measurements [10,93-96]. At low coverages, O$_2$ adsorbs in so-called peroxo and superoxo configurations [9,95], which correspond to adsorption onto threefold hollow and bridge sites, respectively [97,98]. Molecular oxygen bound at low coverages in the peroxo state has been found to dissociate on Pt(111) even at 96 K [9,95] although dissociation is slow at this temperature. As the coverage of O$_2$ increases, the a majority of the O$_2$ resides in the superoxo state., and at the saturation coverage of 0.44 ML the dissociation of O$_2$ on Pt(111) is no longer observed at surface temperatures below about 92 K [9].

The increase in the dissociation probability of O$_2$ observed when increasing the surface temperature during the $^{16}$O-atom exposure may simply indicate that O$_2$ thermally dissociates during these experiments. As discussed above, the thermal dissociation of O$_2$ on Pt(111) has been observed at surface temperatures below 110 K when the O$_2$ coverage
is below saturation [9,95]. Thus, thermal dissociation could occur during the beam experiments if the displacement of $^{18}$O$_2$ from the surface generated enough unoccupied sites to accommodate the $^{18}$O atoms resulting from dissociation of adsorbed $^{18}$O$_2$ molecules.

Arguments against this are as follows. Firstly, the flux of $^{16}$O$_2$ from the beam is approximately 20 times the $^{16}$O-atom incident flux so the adsorption of $^{16}$O$_2$ could compete effectively with $^{18}$O$_2$ dissociation for empty surface sites, depending on the characteristic timescales for these processes. Additional evidence that thermal dissociation of $^{18}$O$_2$ is negligible in these experiments is the observation that the dissociation yield nearly doubles at $T_s = 110$ K when the $^{16}$O-atom fluence is increased from 0.1 to 0.2 ML (i.e. 20 to 40 seconds). If empty sites are created during $^{18}$O$_2$ displacement, and the observed dissociation of $^{18}$O$_2$ is due to thermal activation of molecules adjacent to these sites, then dissociation should continue during the approximately 10 minute time period that passes between termination of the beam exposure and the start of the subsequent TPD measurement. Thus, a factor of about two increase in the $^{18}$O$_2$ dissociation yield observed when the $^{16}$O-atom exposure is prolonged by only 20 seconds cannot be easily explained by thermally activated dissociation since prior experiments indicate that this reaction is quite slow at surface temperatures of 110 K and below. Finally, the observation that $^{18}$O$_2$ dissociation continues to occur up to total O-atom coverages of $\sim$0.40 ML is perhaps the most compelling evidence to support a nonthermal or dynamic mechanism for $^{18}$O$_2$ dissociation during $^{16}$O-atom adsorption. It is well known that O$_2$ does not dissociate thermally on Pt(111) in UHV at O-atom coverages greater than 0.25 ML.
The dissociation of O_2 observed in this study appears to be a nonthermal process that competes with the nonthermal displacement of O_2 that is stimulated by the adsorption of oxygen atoms incident from the gas-phase. These reactions may be represented by Equations 3-2 and 3-3 shown below.

\[ 16O_{(\text{gas})} + 18O_2_{(\text{ad})} \rightarrow 16O_{(\text{ad})} + 18O_2_{(\text{gas})} \]  
\[ 16O_{(\text{gas})} + 18O_2_{(\text{ad})} \rightarrow 16O_{(\text{ad})} + 2^{18}O_{(\text{ad})} \]  

Here, Equation 3-2 depicts the dynamic displacement (not including thermal O_2 desorption) of \( ^{18}O_2 \) and Equation 3-3 represents dynamic dissociation of \( ^{18}O_2 \) caused by a gas-phase \( ^{16}O \)-atom. One would intuitively expect that the rate of the dynamic displacement and dissociation could be expressed in the following manner:

\[ Rate_E = \sigma \phi \theta_{18O_2} \]  
\[ Rate_D = k \phi \theta_{18O_2} \left( 1 - \frac{\theta_O}{\theta_c} \right) \text{ for } \theta_O < \theta_c \]  

where \( Rate_E \) and \( Rate_D \) denote the nonthermal \( ^{18}O_2 \) evolution and dissociation rates. The cross-section for nonthermal displacement is denoted as \( \sigma \). A simple rate expression is assumed in Equation 3-5, however, the dependence on \( \theta_O \) is not known. The temperature dependence of the dynamic displacement rate is assumed to be separable and in the form of a rate constant represented by \( k \) in Equation 3-5. Other parameters are denoted as follows: \( \phi \) is the \( ^{16}O \)-atom flux onto the surface, \( \theta_{18O_2} \) is the fractional coverage of \( ^{18}O_2 \), \( \theta_O \) represents the total fractional coverage of adsorbed oxygen atoms (\( \theta_{16O} + \theta_{18O} \)), and \( \theta_c \) is the critical O-atom coverage at which the dissociation process ceases. An analysis of the rate data can be performed to determine the relative rates of desorption and dissociation. This method may be complicated when \( \theta_O > 0 \) due to the thermal desorption
of $^{18}$O$_2$. The analysis will then be focused around the initial rate data. It is not possible to determine the initial dissociation rate experimentally due to the limitations imposed upon using TPD. The dissociation yield data derived from TPD measurements can be approximated by calculating an average dissociation rate, by dividing the dissociation yield by the duration of time over which dissociation occurs (40 seconds). The initial evolution and dissociation rates are recorded along with a sum of these rates in Table 3-2.

The initial displacement rates shown are consistent with the findings of Wheeler et al. [16] where they observed the initial desorption probability (desorption rate/$^{16}$O-atom flux) on the order of 0.4-0.5. As the surface temperature increased, marginal increases in the initial evolution rate were observed. The dissociation rate increase is more pronounced with increasing surface temperature. Experiments performed with a surface temperature $\geq$ 100 K showed that for every $^{16}$O-atom impinging on the surface, at least one $^{18}$O$_2$ molecule was displaced or dissociated. Assuming that the reaction rate Equations 3-2 and 3-3 capture this chemistry, one would anticipate that the $^{18}$O$_2$ evolution rate would decrease as the dissociation yield increases. However, the initial displacement probability remained approximately constant.

An explanation may be attributed to the two adsorption geometries of adsorbed O$_2$ onto Pt(111). With an $^{18}$O$_2$ coverage of 0.44 ML and a surface temperature of 77 K, the molecule is known to reside predominately at the bridge site. Molecular oxygen can also reside at a threefold hollow site, where the O-O bond is weaker than that of the superoxo oxygen [95]. As the surface is heated to about 140 K, the superoxo adsorbed molecular oxygen will desorb, and simultaneously pass through the peroxo state and decompose into oxygen atoms. It is possible that the gaseous $^{16}$O-atoms may be interacting with two
different types of adsorbed O$_2$ species, and that the relative populations of these species vary with temperature. Since the peroxo species has a lower O-O bond strength, this species may tend to decompose when exposed to oxygen atoms, whereas the superoxo species may be more prone to desorb.

The temperature dependence of the dissociation process may provide information regarding the activation energy required to convert the superoxo species into the peroxo state. Temperature programmed desorption provides the total dissociation yield of molecular oxygen under the reaction conditions examined. By definition, the total dissociation yield is the integral of the rate expression in Equation 3-5 over time yields Equation 3-6.

\[
yield = \int k(T) \phi \theta_{O_2} \left( 1 - \frac{\theta_{e}}{\theta_{c}} \right) dt
\]

Equation 3-6 makes the assumption that the temperature dependent component is separable and in the form of a rate constant. Also, with the knowledge that the thermal desorption of $^{18}$O$_2$ is on the order of 10%, then the ratio of the dissociation yields between two temperatures would be approximately equal to the ratio of the rate constants. This would provide a means for measuring the average activation energy of dissociation via the following expression.

\[
\frac{\text{yield}_{T_1}}{\text{yield}_{T_2}} = \frac{ue^{-Ea/kT_1}}{ue^{-Ea/kT_2}}
\]

Using the information in Table 3-1, an apparent activation energy for dynamic dissociation was found in the range of 2.8-3.3 kJ/mol. Recent \textit{ab initio} calculations suggest that this barrier should be about 14 kJ/mol [98]. The activation barrier would most certainly be influenced by the local atom and molecule coverages, which could
explain the differences between these values. Recall that the dissociation channel deactivates after the first 40 seconds (0.2 ML $^{16}$O-atoms) of the exposure, showing that the activation energy is a function of $\theta_O$. The limitations imposed using TPD makes it difficult to resolve the activation energy for molecular oxygen dissociation as a function of $\theta_O$, in coverage ranges where molecular oxygen decomposes thermally. The calculated activation energy is then an average activation energy over the entire range of $0 < \theta_O < 0.44$ ML. The calculated activation energy obtained is very small when compared with heats of adsorption for O/Pt(111) (350 kJ/mol) [14]. The incoming O-atoms have more than enough energy to overcome this barrier. A more likely interpretation of this data is that the apparent activation energy is the barrier required for the superoxo species to be converted into the peroxo species on the surface, with the zero point taken to be the Pt(111) surface covered with $^{18}$O$_2$ in the superoxo state. The oncoming $^{16}$O-atom then effectively interacts with two different forms of molecular oxygen, one with high probability of displacing (superoxo), and the other more likely to dissociate (peroxo).

3.5 Conclusions

Dynamic displacement and dissociation of $^{18}$O$_2$ adsorbed on Pt(111) was observed when exposed to beam of gaseous $^{16}$O-atoms. The displacement rate maximum increased with surface temperature, while the total desorption yield decreased with increasing surface temperature. Subsequent temperature programmed desorption measurements revealed that the balance of $^{18}$O$_2$ decomposed on the surface through a dynamic dissociation event. The dissociation increased with surface temperature and the initial dissociation probabilities (dissociation rate / $^{16}$O-atom flux) are estimated as 0.3, 0.4 and
0.6 for surface temperatures of 90, 100 and 110 K respectively. For the dissociation
yields an apparent activation energy for dissociation is estimated as ~3 kJ/mol, which is
only about 1% of the $^{16}$O-atom adsorption energy (350 KJ/mol) on a clean Pt(111)
surface. The temperature dependence of the dissociation probability and the low
activation energy for dissociation were interpreted as evidence for shifts in the relative
populations of the O$_2$ from superoxo to peroxo states with increasing temperature, with
the superoxo species favoring desorption and the peroxo species tending to dissociate.

Table 3-1. Displacement and desorption yields of $^{18}$O$_2$ when exposed to $^{16}$O-atoms while
holding the temperature at 90, 100 and 110 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\theta_{18O2}$ dissociated (ML)</th>
<th>$\theta_{18O2}$ displaced (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.06</td>
<td>0.38</td>
</tr>
<tr>
<td>100</td>
<td>0.08</td>
<td>0.36</td>
</tr>
<tr>
<td>110</td>
<td>0.11</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Table 3-2. Initial evolution rate, the estimated initial dissociation rate, and the sum of the
two rates when exposing an $^{18}$O$_2$ saturated on Pt(111) to a beam with a flux
of 0.005 ML/sec of $^{16}$O-atoms.

<table>
<thead>
<tr>
<th>Ts (K)</th>
<th>Initial evolution rate (ML/s)</th>
<th>Estimated dissociation rate (ML/s)</th>
<th>Sum of evolution and dissociation rate (ML/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.0024</td>
<td>0.0015</td>
<td>0.0039</td>
</tr>
<tr>
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<td>0.0025</td>
<td>0.0020</td>
<td>0.0045</td>
</tr>
<tr>
<td>110</td>
<td>0.0027</td>
<td>0.0030</td>
<td>0.0057</td>
</tr>
</tbody>
</table>
Figure 3-1. Partial pressure traces of $^{18}$O$_2$ desorbing from Pt(111) when exposed to $^{16}$O-atoms with a surface temperature of 90, 100 and 110 K.
Figure 3-2. Temperature programmed desorption spectra taken after precovering the Pt(111) surface with $^{18}$O$_2$ and exposing this surface to $^{16}$O-atoms. The left panel shows the desorption traces of mass 32, 34 and 36 when the exposure was conducted at 90 K. The right panel shows a comparison of the mass 34 spectra taken after exposing this surface to 1.8 ML of $^{16}$O-atoms at 90, 100 and 110 K.
Figure 3-3. Normalized dynamic displacement beam traces of $^{18}\text{O}_2$ when exposed to a $^{16}\text{O}$-atom beam interrupted every thirty seconds, taken while holding surface temperatures at 90 and 110 K.
CHAPTER 4
CARBON MONOXIDE OXIDATION FROM HIGH OXYGEN COVERAGE PHASES ON Pt(111)

The oxidation of carbon monoxide was investigated from high coverage phases of oxygen on Pt(111) generated through O-atom beam exposures. Carbon monoxide was found to adsorb onto oxygen covered Pt(111) held at 100 K, with oxygen coverages in the range of 0.25-0.6 monolayer (ML). The total CO uptake was found to be independent of $\theta_O$ and is on the order of 0.30 ML. Carbon monoxide adsorption onto platinum oxide was not observed. Temperature programmed reaction measurements conducted on surfaces with CO coadsorbed with oxygen atoms show that CO reacts with all oxygen states on Pt(111), but preferentially reacts with the oxygen atoms having the weakest oxygen atom-platinum binding strength. Isothermal CO oxidation experiments were conducted on Pt(111) with initial oxygen coverages in the range of 0.25-0.6 ML and from platinum oxide. The partial pressure CO$_2$ traces from high oxygen coverage phases taken at surface temperatures of 300, 400 and 500 K each had similar features. Each rate curve was characterized by an immediate jump in the CO$_2$ partial pressure, an increase to a rate maximum and finally a decay to the baseline, which is consistent with a precursor adsorption mechanism. The overall reaction rate increased with surface temperature. The oxidation of carbon monoxide on platinum oxide exhibited inherently different kinetic behavior from that observed for coverages of chemisorbed oxygen atoms. Initially, the CO$_2$ formation rate was very low, after a delay, the rate gradually increased to a maximum, then finally decayed to the baseline.
4.1 Introduction

Platinum is known for its catalytic activity towards oxidizing carbon monoxide [21-40,99]. Despite numerous studies performed on CO oxidation on platinum surfaces, the development of a mechanistic understanding of this reaction remains a challenge. One contribution to this problem is the difficulty in generating atomic oxygen coverages on Pt(111) greater than 0.25 monolayers (ML) under UHV conditions, where 1 ML is defined as the Pt(111) surface atom density of $1.505 \times 10^{15} \text{ cm}^{-2}$, so that detailed investigations of the reactivity of different forms of atomic oxygen can be performed. Recently, higher oxygen atom coverages on Pt(111) have been generated when exposing Pt(111) to active oxidants such as ozone, NO$_2$ and oxygen atoms [51,52,55]. This capability affords an opportunity to both advance the fundamental understanding of the Pt-catalyzed CO oxidation reaction and to characterize the reactivity of oxygen atoms in high-coverage phases on Pt surfaces.

The interactions of O$_2$ with the Pt(111) surface have been studied in detail. It is known that O$_2$ chemisorbs on Pt(111) and generates a saturation coverage of 0.44 ML [15]. Heating O$_2$-saturated Pt(111) results in O$_2$ desorption at about 140 K, as well as dissociation to produce 0.25 ML of oxygen atoms chemisorbed on the surface, which is the maximum O-atom coverage that can be generated on Pt(111) using O$_2$ in UHV. These oxygen atoms become mobile at a temperature of about 200 K, and organize into islands with a p(2x2) structure in which the O-atoms bind at fcc hollow sites [52,100]. Raising the sample temperature to ~750 K causes the adsorbed oxygen atoms to recombine and desorb [9,12]. High surface coverages of oxygen atoms have been formed by electron dissociation of O$_2$/Pt(111) [9,50], and by exposing Pt(111) to NO$_2$ [51-53], O$_3$ [54,55], and O-atoms [56]. Recently, we successfully generated atomic oxygen...
coverages as high as 2.9 ML on Pt(111) using a beam of oxygen atoms. The development and properties of the resulting surface oxygen phases were investigated in detail using several analytical techniques.

As the coverage of oxygen atoms on the Pt(111) surface exceeds 0.25 ML, the onset of O2 desorption is observed to shift to lower temperatures in temperature programmed desorption (TPD) experiments. Two distinct desorption features are observed at temperatures (~550 and 640 K) below that for O2 desorption at O-atom coverages less than 0.25 ML, indicating that the O-Pt(111) binding energy decreases significantly as the O-atom coverage increases in this range. Increasing the O-atom coverage beyond about 0.75 ML is accompanied by a decrease in the O2 desorption rate at low temperature, and the development of a single sharp desorption feature that shifts toward higher temperature as the O-atom coverage is increased. Using X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (ELS) measurements in conjunction with TPD, the sharp desorption feature could be attributed to the growth of Pt oxide domains on Pt(111) at coverages above 0.75 ML.

The adsorption of CO on Pt(111) has been studied extensively [26,94,101-104]. On clean Pt(111), CO adsorbs on both atop and bridge sites of Pt(111), and reaches saturation coverages of 0.5 and 0.66 ML at surface temperatures of 300 K and 100 K, respectively. At room temperature, CO is distributed equally between atop and bridge sites. The mechanism for CO oxidation on Pt(111) with less than 0.25 ML involves several steps, including the molecular adsorption of CO and the dissociative adsorption of O2, the diffusion of CO and O on the surface, and reaction between CO and O to produce CO2. Recently, a CO2 precursor has also been identified on Pt(111) [32]. Using single
crystal adsorption calorimetry, Yeo et al. found that the initial sticking probability of CO onto Pt(111) was enhanced by the presence of adsorbed oxygen atoms, consistent with a precursor-mediated mechanism for CO adsorption [22]. High resolution XPS and ELS studies revealed that the oxygen atoms block the bridge sites, leaving only atop sites for CO adsorption [31,105], which is consistent with density functional theory calculations (DFT) [27,34]. At 120 K, CO oxidation does not occur on Pt(111) and CO accumulates on the O-covered surface, reaching a coverage of approximately half of that achieved on the clean surface [31,34].

In the temperature range of 270-300 K, the presence of CO on the surface enhances O-atom migration into islands [25]. Based on results of high resolution XPS, CO oxidation was postulated to occur at the boundaries of p(2x2) O-atom islands [31], which is consistent with real-time scanning tunneling microscopy (STM) measurements [23]. Above 400 K, the CO₂ formation rate is primarily determined by the CO impingement rate on the surface [21].

With the ability to prepare high-coverage oxygen phases, including Pt oxide, on Pt(111) under UHV conditions, the basic understanding of Pt-catalyzed CO oxidation can now be extended to include atomic oxygen coverages and phases that are certain to be important under conditions relevant to many industrial applications, such as CO oxidation in oxygen-rich environments. In this study, the oxidation of CO on oxygen-covered Pt(111) was investigated in UHV over a wide range of initial atomic oxygen coverages using temperature programmed reaction (TPR), isothermal kinetic measurements, and low energy electron diffraction (LEED) to gain insights into the mechanism for CO
oxidation on different phases of oxygen on Pt(111) and to characterize the reactivity of different states of oxygen on this surface.

4.2 Experimental Methods

The experiments were conducted in a three-level UHV chamber that reaches a base pressure less than $2 \times 10^{-10}$ Torr, as described in Section 1.3. Briefly, the chamber is evacuated by an ion pump (400 l/sec), a turbo molecular pump (210 l/sec) and a titanium sublimation pump that is inserted into a liquid nitrogen cooled cryoshield. The upper level of the chamber houses a hemispherical analyzer (Specs EA10 plus), a dual Al/Mg anode X-ray source, a variable-energy electron source and an ion sputter source, which provides capabilities for performing X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (ELS) and low energy ion scattering spectroscopy (LEISS) as well as surface cleaning by ion sputtering. The middle level of the chamber is designed primarily for gas-dosing, and contains a directed doser connected to a leak valve as well as a calibrated molecular beam doser. The lower level of the chamber houses a low energy electron diffraction (LEED) optics, a two-stage differentially-pumped plasma beam source and a quadrupole mass spectrometer (QMS).

The Pt(111) crystal that was used in this study is a circular disk (10 mm x 1.5 mm) that was cut and polished to within $0.1^\circ$ of the (111) plane. The crystal was spotwelded to Ta wires and attached to a copper sample holder that is in thermal contact with a liquid nitrogen cooled reservoir. A type K thermocouple was spotwelded to the back side of the crystal to measure the sample temperature. The sample was heated resistively and the sample temperature was controlled using a PID controller to vary the output of a programmable DC supply that delivers power to the sample for heating. The surface temperature could be varied from about 90 to 1200 K with this configuration. The
sample was initially cleaned by sputtering with 600 eV Ar+ ions at a surface temperature of 500 K, followed by annealing for several minutes at 1000 K. Subsequent cleaning involved exposing the Pt sample to O2 for several minutes at 800 K, followed by flashing the sample to about 1000 K to desorb oxygen and carbon oxides. The sample was considered to be clean when no contaminants could be detected with AES, and a sharp, hexagonal (1x1) LEED pattern was observed.

Beams containing oxygen atoms were generated using a microwave plasma source that is mounted in a two-stage differentially-pumped chamber attached to the main UHV chamber. Pure O2 (BOC gases, 99.999%) is continuously supplied to the discharge chamber of the plasma source and partially dissociated in a microwave plasma. Species exit the discharge chamber through small holes, and form a beam that is directed into the UHV chamber. In the first pumping stage, the beam passes between oppositely charged parallel plates (±10 kV/cm) that deflect ions and electrons from the beam. After flowing through a conical skimmer (ϕ = 3 mm) separating the first and second pumping stages, the species travel down a quartz tube before entering the UHV chamber. The quartz tube is 60 mm long and has an inner diameter of 6 mm. A mechanical shutter is located in the first pumping stage to enable control over beam introduction into the main UHV chamber. Mass spectrometric analysis indicates that beams containing about 6% O- atoms in a balance of O2 are generated under the typical plasma conditions employed, and that O-atom fluxes of ~3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1} reach the Pt(111) surface when the sample is rotated 45° off normal to the beam and located about 50 mm from the end of the quartz tube.
A calibrated molecular beam doser was employed to generate a CO (Praxair 99.99\%), beam the design of which closely follows the design given by Yates [57]. The distance between the sample and the doser was set to 1.5 cm to ensure a uniform beam profile across the crystal face. The mass spectrometer was placed away from the beam region to ensure that the partial pressure traces did not contain any artifacts due to reflection of molecules from the surface. Unless otherwise specified, the CO$_2$ pressure traces shown are the original data. The calculated reaction rate data was obtained first by smoothing the beam data with a 5 point adjacent averaging method, followed by a background subtraction.

4.3 Results

4.3.1 Carbon Monoxide Adsorption and TPR on O Precovered Pt(111) Surfaces

High-coverage oxygen phases were generated by exposing the Pt(111) surface to the oxygen atom beam while holding the sample temperature fixed at 450 K. Shown in Figure 4-1 are O$_2$ temperature programmed desorption (TPD) traces obtained after adsorbing different amounts of atomic oxygen using the beam. The TPD trace corresponding to an initial O-atom coverage of 0.25 ML exhibits a single, broad feature, labeled as the $\gamma$ desorption feature. It is well known that the $\gamma$ feature arises from the recombinative desorption of oxygen atoms initially adsorbed in ordered p(2x2) domains on Pt(111) [9,12,14]. As the atomic oxygen coverage increases beyond 0.25 ML, two distinct features, labeled as $\alpha$ and $\beta$, appear at desorption temperatures below that observed for the $\gamma$ feature. The $\alpha$ and $\beta$ features continue to grow in intensity as the oxygen coverage increases to about 0.75 ML. The development of the $\alpha$ and $\beta$ features indicates that the average O-Pt(111) binding energy decreases with increasing oxygen
coverage up to 0.75 ML. From leading edge analysis of the TPD traces, our group found that the desorption activation energy is estimated to decrease from ~190 to 120 kJ/mol as the oxygen coverage increases from 0.25 to 0.75 ML. Prior work indicates that oxygen atoms begin to adsorb in hcp hollow sites at coverages greater than 0.25 ML [52], at which the binding energy is about 50 kJ/mol lower than at the fcc hollow site [34] – the preferred O-atom binding site at Θ < 0.25 ML. Closer packing in the chemisorbed layer also results in stronger lateral repulsive interactions between adsorbed oxygen atoms as the coverage increases. Both of these factors lower the average O-Pt(111) binding energy.

The order in which the desorption features appear with increasing coverage shows that oxygen atoms first arrange into a p(2x2) structure, and that the surface saturates with these domains before more repulsive states are generated on the surface. In contrast, as the coverage increases beyond 0.25 ML, the lowest temperature α state appears before the β state saturates, suggesting that oxygen atoms adsorb in distinct repulsive environments in this coverage range, rather than sequentially populating each environment as coverage increases. We note, however, that the α feature grows in intensity much more sharply as the oxygen coverage increases beyond 0.50 ML, than over the 0.25 to 0.50 ML range (Figure 4-1). As discussed previously, the β feature appears to arise predominantly from the desorption of oxygen atoms initially adsorbed in hcp hollow sites, which form (2x2) domains with a “honeycomb” structure and a local coverage of 0.50 ML [51]. We attributed the α feature to desorption of oxygen initially adsorbed in disordered domains of local concentration greater than 0.50 ML, in which the O-surface binding energy is apparently weaker than in the honeycomb domains. If this
interpretation is correct, the TPD results indicate that the disordered domains form in small quantities at total coverages below 0.50 ML, and grow more rapidly once the total coverage exceeds 0.50 ML.

Islands of platinum oxide grow on the Pt(111) surface when the atomic oxygen coverage increases above about 0.75 ML [55]. As the initial amount of oxide on the surface increases, the O$_2$ desorption rate maximum shifts toward higher temperature and sharpens dramatically, giving rise to explosive O$_2$ desorption. A TPD spectrum obtained from an oxidized Pt(111) surface, initially covered with 1.7 ML of oxygen atoms, is shown in the right panel of Figure 4-1 along with a desorption spectrum obtained from 0.25 ML of O-atoms chemisorbed on Pt(111). The maximum desorption rate is more than 50 times greater from the oxide-covered surface than from the surface with 0.25 ML of O-atoms, and the desorption peak is centered at a higher temperature than both the $\alpha$ and $\beta$ features. Notice also that the trailing edges of the desorption features are virtually identical in Figure 4-1. This suggests that 0.25 ML of chemisorbed oxygen atoms on Pt(111) are in similar arrangements on the surface, and therefore experience similar bonding environments, regardless of whether the 0.25 ML coverage is generated by adsorbing oxygen on the initially clean surface or by desorbing oxygen from high-coverage oxygen phases.

Temperature programmed reaction (TPR) experiments were performed to characterize the reactivity of the surface oxygen toward CO. In these experiments, atomic oxygen coverages of 0.25, 0.39, 0.59 and 1.7 ML were generated on the Pt(111) sample using the atomic oxygen beam, and the surface was then held at 100 K and saturated with CO supplied from the calibrated beam doser. TPR measurements were
then conducted using a heating rate of 3 K/sec, and monitoring the partial pressures of CO, CO$_2$ and O$_2$. No other species were observed to desorb in these experiments. Carbon monoxide did not adsorb on the Pt(111) surface covered with 1.7 ML of oxygen atoms at a surface temperature of 100 K, indicating that CO binds very weakly on Pt oxide.

The TPR spectra obtained from the surface initially covered with 0.25 ML of O-atoms reveal that the oxygen atoms are completely converted into CO$_2$ and that excess CO desorbs from the surface. For initial atomic oxygen coverages between 0.25 and 0.60 ML, CO, CO$_2$ and O$_2$ were all observed to desorb from the surface, indicating that a fraction of the adsorbed CO and O-atoms do not react at these initial coverages. Figure 4-2 shows a TPR spectrum obtained from Pt(111) initially covered with 0.39 ML of O-atoms and a saturation amount of CO. Carbon dioxide is found to desorb in a single peak centered at 300 K, and the background CO$_2$ pressure was observed to continuously increase during the temperature ramp due to CO$_2$ desorption from the sample holder and the Ta support wires. Two CO desorption features are also observed at temperatures of ~415 and 500 K. The high temperature feature is known to arise from CO molecules desorbing from surface defect sites, which are apparently unreactive toward oxygen adsorbed on Pt(111) [21]. The observation of CO desorption at 415 K during these experiments indicates that a fraction of the CO adsorbed on Pt(111) terrace sites does not react with the chemisorbed oxygen atoms either. Finally, O$_2$ desorbs in a single feature centered near 680 K, consistent with oxygen present on the surface in p(2x2) domains once CO is completely removed from the surface.
These results show that a fraction of the adsorbed CO and O-atoms do not react, even though CO is present on the surface in a limiting concentration, as shown below. The strong binding of CO at defect sites may render these molecules relatively unreactive toward the adsorbed oxygen atoms; however, about half of the CO that does not react resides in a more weakly bound state on the terraces. Previous workers have suggested that CO binding to Pt(111) is destabilized by chemisorbed O-atoms, causing the oxidation reaction to occur readily at initial oxygen coverages near 0.25 ML [21]. As the oxygen coverage decreases and isolated oxygen atoms are generated during CO oxidation, the CO binding to the surface strengthens and the CO apparently becomes less reactive toward the surface oxygen.

The TPR spectra were analyzed to determine the coverage of CO adsorbed on the surface before and after reaction as a function of the initial oxygen coverage as well as the amount of oxygen remaining on the surface after reaction. To convert the integrated TPD areas into surface coverages, we obtained and integrated TPD spectra from well-established saturation coverages of 0.25 and 0.65 ML of O [9,14,51] and CO [26] generated on Pt(111), respectively, by the dissociative chemisorption of O2, and separately from CO adsorption at a surface temperature of 100 K. The analysis neglects variation in the sensitivity of the mass spectrometer throughout the day, which was found to be a reasonable approximation based on the reproducibility of integrated intensities of the TPD obtained from the saturation O and CO coverages stated above. Finally, the analysis assumes that the CO and O are removed from the surface only by desorption and reaction to generate CO2. For the analysis, the oxygen coverages before and after reaction are determined directly from the O2 TPD data, and the CO coverage remaining
on the surface after reaction is also calculated from the CO desorption trace. Since the CO\textsubscript{2} background pressure increased continuously during the TPR measurements, we chose to calculate the amount of CO molecules that are oxidized to CO\textsubscript{2} by computing the difference between the oxygen coverages obtained before and after reaction.

Table 4-1 shows the initial CO and O coverages as well as the amounts of O and CO that do not react as a function of the initial O-atom coverage. The analysis shows that the saturation CO coverage at 100 K decreases from 0.65 to 0.31 ML when \( \Theta_o \) increases from 0 to 0.25 ML, which is in agreement with previous findings \([31,100]\). The saturation CO coverage decreases remains constant, within the experimental uncertainty, as the initial oxygen coverage increases to 0.59 ML. The decrease in the CO saturation coverage to about half its value on the clean surface for an oxygen coverage of 0.25 ML is known to be caused by O-atoms blocking CO adsorption on bridge sites, limiting CO adsorption to only atop sites \([31,105]\). The invariance of the CO saturation coverage as the O-atom coverage increases from 0.25 to about 0.60 ML indicates that oxygen atoms chemisorbed at these higher coverages do not appreciably impede CO adsorption on atop sites. Although we did not investigate CO adsorption at oxygen coverages other than those listed in the table, the inability of CO to adsorb on the oxidized surface at \( T_s = 100 \) K suggests that the CO saturation coverage decreases as the fraction of the surface covered by oxide particles increases.

The TPR data also provides insights into the relative reactivity of the different surface oxygen phases. Table 4-1 shows that 0.33 ML of the adsorbed O-atoms do not react with CO during the TPR experiment performed with 0.30 ML of CO initially co-adsorbed with 0.59 ML of oxygen. Shown in the left panel of Figure 4-3 are O\textsubscript{2} TPD
spectra obtained during the TPR experiment and from the surface initially covered with 0.59 ML of oxygen atoms. As may be seen in the figure, the conversion of CO to CO$_2$ is accompanied by a decrease in each of the O$_2$ desorption features, with the largest decrease in the low temperature $\alpha$ feature. The trailing edge of the desorption trace is also lower in the TPD spectrum obtained after CO oxidation. For an initial oxygen coverage of 0.59 ML, the surface is believed to be covered with oxygen atoms in both disordered domains and high-coverage ordered domains, and the amount of O$_2$ desorbing in the $\alpha$ and $\beta$ features is assumed to be proportional to the initial concentrations of oxygen atoms in these phases. The latter assumption considers the conversion of oxygen atoms from the disordered phase to the high-coverage ordered phase to be negligibly slow during the TPD experiment. In this case, the larger decrease in the $\alpha$ feature suggests that O-atoms associated with the disordered domains are more reactive than those present in the high-coverage ordered domains. This conclusion is reasonable in light of the lower binding energy of oxygen in the disordered phase, as suggested by the TPD results (Figure 4-1).

However, if the rate of oxygen interchange between phases is appreciable during TPD, then the relative decreases in the O$_2$ desorption features observed after reaction with CO will not provide a simple measure of the relative reactivity of the different oxygen phases. For example, each phase may be equally reactive toward CO, but a fraction of the oxygen in the more repulsive disordered phase may be converted to a more stable phase during TPD. This would cause the amount of oxygen desorbing in the $\alpha$ feature to be less than that remaining on the surface after reaction with CO at lower temperature (~300 K).
A comparison of the O$_2$ TPD spectra obtained from surfaces with similar initial oxygen coverages, but prepared in different ways, suggests that oxygen atoms are fairly immobile at temperatures near those that produce O$_2$ desorption. As shown in Table 4-1, the surface is covered with 0.33 ML of oxygen atoms at the end of the TPR experiment in which a saturation coverage of CO was initially co-adsorbed with 0.59 ML of O-atoms on Pt(111). Shown in the right panel of Figure 4-3 are the O$_2$ TPD spectra obtained during this TPR experiment and that obtained from a surface on which 0.25 ML of oxygen atoms were adsorbed by dissociating O$_2$ on the surface. The spectrum obtained in the TPR experiment shows that the 0.33 ML of oxygen atoms remaining after CO oxidation desorb in varying amounts in the $\alpha$, $\beta$, and $\gamma$ desorption states, whereas only the $\gamma$ desorption feature is observed in the spectrum obtained from an initial oxygen coverage of 0.25 ML prepared by molecular oxygen adsorption.

This shows clearly that the distribution of oxygen phases or states is not only a function of the oxygen coverage, but is also dependent upon the manner in which that coverage is obtained. Since the $\gamma$ feature is not saturated in the TPD spectrum obtained after CO oxidation, the migration of oxygen atoms to more energetically favorable states must be slow at the temperatures for recombinative O$_2$ desorption. Jerdev et al. [52] have also reported evidence that O-atoms adsorbed at high coverages on Pt(111) have limited mobility at these surface temperatures. Since the adsorbed O-atoms are found to be relatively immobile on the surface, the decrease in the $\alpha$ desorption feature after reaction with CO is consistent with oxygen atoms in the high-coverage disordered phase being more reactive toward CO than are the more strongly-bound oxygen species.
When considering all of the observations in this section, the following points can be made. First, CO does not appreciably adsorb onto the platinum oxide, even at 100 K. The total CO uptake is a strong function of O-atom coverage in the range of \(0<\theta_0<0.25\). After this point, the saturation coverage of CO is independent of \(\theta_0\). This data suggests that the additional oxygen atoms adsorbed beyond 0.25 ML do not block the sites needed for CO adsorption. Since CO is known to only adsorb onto atop sites on Pt(111) \[31,34\], it is reasonable to conclude that chemisorbed oxygen atoms do not impede CO adsorption at atop sites. This is consistent with recent reports that chemisorbed O-atoms bind at fcc and hcp hollow sites up to high O-atoms coverages \[52\]. During TPR, carbon monoxide was found to preferentially react with the oxygen atoms in disordered domains, which gives rise to the \(\alpha\) desorption state. Finally, the oxygen desorption features observed are sample history dependent. This is an indication that the oxygen atoms do not efficiently migrate out of these domains toward sites that are more thermodynamically favored, which is in agreement with observations made by Jerdev et al. \[52\].

### 4.3.2 CO Oxidation on High-Coverages of Chemisorbed Oxygen Atoms Under Isothermal Conditions

The oxidation of CO by oxygen atoms chemisorbed on Pt(111) was investigated under isothermal conditions using direct rate measurements. Atomic oxygen coverages in the range of 0.25 to 0.50 ML were generated on the surface using the atomic oxygen beam, and CO oxidation was investigated on these layers at surface temperatures of 300, 400 and 500 K. In the direct rate measurements, the O-covered surface is held at constant temperature and exposed to a CO molecular beam of known flux while monitoring the temporal evolution of the CO\(_2\) partial pressure with the mass spectrometer. As discussed in Section 4.2, this experiment provides a direct measure of the rate of CO\(_2\) production as
a function of the surface oxygen coverage since oxygen is continuously removed from the surface during reaction. Additionally, since the surface is maintained at a constant temperature, the direct rate measurements also aid in separating the effects of surface coverage and temperature on the CO oxidation kinetics.

The temporal evolution of the CO₂ production rate exhibits similar characteristics for all the surface temperatures investigated and initial oxygen coverages less than 0.60 ML (Figures 4-4 to 4-6). In each measurement, the CO₂ production rate increases abruptly when the CO beam exposure to the surface is initiated. The reaction rate then increases toward a maximum during an induction period, and decays thereafter to a steady level. Oxidation of CO at the chamber walls causes the final CO₂ partial pressures to remain greater than the values obtained before introducing CO into the UHV chamber. Although not shown in the figures, the CO₂ pressure rapidly returns to its initial value when the CO flow into the chamber is terminated. Additionally, the final CO₂ pressures vary among the measurements shown mainly because the rate curves were obtained using slightly different CO fluxes, as indicated in the figures. After each direct rate measurement was completed, TPD was performed to characterize the species remaining on the surface. Neither O₂ nor CO₂ was detected by TPD after any of the direct rate experiments, which indicates that all of the adsorbed oxygen atoms are converted to CO₂ by reaction with CO under the conditions investigated.

The CO₂ production rate at a surface temperature of 300 K is shown in the left panel of Figure 4-4 as a function of monolayers (ML) of CO exposed to the surface for initial atomic oxygen coverages θₒ of 0.25, 0.36 and 0.44 ML. The right panel of the figure shows the CO₂ production rate as a function of the oxygen atom coverage, which
was determined by integrating the rate versus time data and setting the $\theta_o$ scale using the known value of $\theta_o^i$. The oxygen coverage $\theta_o(t)$ at any time during reaction is determined from Equation 4-1,

$$\theta(t) = \theta_o^i \left[ 1 - \frac{\int_0^t \Delta P(s) ds}{\int_0^s \Delta P(s) ds} \right]$$

(4-1)

where $\Delta P$ is the partial pressure rise of CO$_2$ from its initial level, or equivalently the CO$_2$ production rate, and $s$ is an integration variable.

Distinct differences are observed in the rate behavior at 300 K measured at the different initial oxygen coverages. Firstly, the maximum reaction rate increases and is reached at larger CO exposures with increasing $\theta_o^i$. Notice that the maximum CO oxidation rate is uncorrelated with the CO fluxes employed, which suggests that the rate of CO oxidation at 300 K is not controlled by the rate of CO adsorption for CO incident fluxes near 0.1 ML/sec. The difference between the maximum and initial reaction rates, $(r^{\text{max}} - r^i)$ also increases with increasing $\theta_o^i$. After passing the maximum, the reaction rate decreases rapidly but shortly thereafter the rate curve exhibits an inflection point after which the decline in the rate slows down. The reaction rate then decreases more rapidly and reaches its terminal value after no more than 20 ML of CO has impinged on the surface. Note that the CO desorption rate is negligible at a surface temperature of 300 K relative to the adsorption rate for CO incident fluxes near 0.1 ML/sec. Thus, the surface coverage of CO will reach high values at 300 K if CO oxidation is also slower than adsorption, which appears to be the case.
An induction period prior to the CO$_2$ production rate maximum has been previously observed in the oxidation of CO over oxide-supported Pd particles [106], and could be explained in that case by invoking a precursor-mediated description of the CO chemisorption probability. In this model, CO first adsorbs into a weakly bound precursor state from which the molecule can either desorb or chemisorb into a more strongly bound state. Adsorption into the precursor state was assumed to occur only on oxygen-covered domains of the surface and the parameters of the model were chosen such that the CO chemisorption probability $s_{CO}$ decreases with increasing surface temperature and atomic oxygen coverage according to Equation 4-2,

$$s_{CO} = s_{CO}^i (1 - \frac{\theta_{CO}}{\theta_{CO}^{sat}} - \nu_{app} \exp(-\frac{E_{app}}{k_B T_s} \frac{\theta_{O}}{\theta_{O}^{sat}}))$$

(4-2)

In agreement with experimental observations of CO oxidation on Pd particles [106], the model predicts that the induction period prior to the rate maximum and the difference between the initial and maximum reaction rates increase with increasing surface temperature. This prediction originates from the inverse relationship between the CO chemisorption probability and the surface temperature that is built into the model. Since the chemisorption probability also decreases with increasing atomic oxygen coverage, the model will correctly predict the general trends in the reaction rate with initial oxygen coverage observed in the present study, namely, the increase in the induction period and the increase in $(r_{max} - r_{i})$ with increasing $\theta_{O}^{i}$.

The change in the slope of the rate curve after the rate maximum is indicative of a sudden increase in the surface coverage of CO due to depletion of oxygen from the surface below a coverage of 0.25 ML. Shown in the right panel of Figure 4-4 are the rate curves plotted as a function of the O-atom coverage, which were obtained by integrating
the rate versus time curves and setting the $\theta_o$ scale with the known value of $\theta_o^i$. Notice that in each case the inflection in the rate curve occurs below an oxygen coverage of 0.25 ML, though not always at the same oxygen coverage. As discussed in Section 4.3.1, the maximum CO coverage $\theta_{CO}$ that can be generated on Pt(111) is relatively insensitive to the O-atom coverage for $\theta_o = 0.25$ to 0.60 ML, at least at 100 K, but $\theta_{CO}$ doubles as $\theta_o$ decreases from 0.25 ML to zero. Thus, as oxygen-free regions are generated on the surface during reaction, the rate of CO adsorption and hence the CO coverage increases more rapidly and offsets the steep decline in the CO$_2$ production rate due to oxygen removal from the surface. Finally, the increase in the maximum reaction rate with increasing $\theta_o^i$ could result from higher oxygen or CO coverages on the surface once the rate maximum is reached.

However, as seen in the right panel of Figure 4-4, the values of $\theta_o$ at the rate maximum (~0.30 ML) do not differ appreciably with increasing $\theta_o^i$. Furthermore, it is unlikely that higher CO coverages are generated since $\theta_{CO}$ is relatively insensitive to a change in oxygen coverage between 0.25 and 0.60 ML. Thus, the increase in $r_{\text{max}}$ with $\theta_o^i$ appears to be most consistent with a slight increase in the intrinsic reactivity of oxygen atoms populating high-coverage domains rather than the low-coverage p(2x2) phase. This conclusion is consistent with the TPR results discussed in Section 4.1.

The production rate of CO$_2$ at a surface temperature of 400 K is shown in Figure 4-5 as a function of CO exposure in the left panel and O-atom coverage in the right panel for initial atomic oxygen coverages of 0.25, 0.37 and 0.45 ML. At $T_s = 400$ K, the induction period prior to the rate maximum and the difference between the initial and maximum reaction rates both increase with increasing $\theta_o^i$ as observed at 300 K.
Characteristics of the rate behavior do change, however, when CO oxidation is conducted at the higher temperature. Interestingly, the induction period obtained at a given $\theta_o^i$ remains largely invariant to an increase in the surface temperature is increased from 300 to 400 K, but the value of $(r_{\text{max}} - r_i)$ does increases with surface temperature in this range. The model for precursor-mediated adsorption predicts that both quantities increase with increasing $T_s$.

Also, the maximum reaction rate no longer increases with increasing $\theta_o^i$ at $T_s = 400$ K, but appears to scale with the incident CO fluxes. This behavior is consistent with the CO adsorption rate beginning to limit the overall CO$_2$ production rate at 400 K. Since the intrinsic rate constant for CO oxidation on the surface increases with increasing surface temperature, while the net CO adsorption rate decreases, the surface reaction will be limited by the CO coverage as the surface temperature is increased. The CO$_2$ production rates are also higher when the surface temperature is increased to 400 K. This may be seen by comparing the values of the maximum reaction rates obtained at 300 and 400 K, and also by noticing that the CO$_2$ production rate falls to its final value after about 15 ML CO is exposed to the surface at 400 K, which is faster than observed at 300 K.

The onset of O$_2$ thermal desorption from high-coverage oxygen phases on Pt(111) occurs at about 500 K so this temperature represents an upper bound at which to investigate the CO oxidation reaction. As may be seen in Figure 4-6, the induction period as well as the value of $(r_{\text{max}} - r_i)$ both increase with increasing $\theta_o^i$. The induction period for a given $\theta_o^i$ is also approximately the same as that observed at lower surface temperatures. However, the values of $(r_{\text{max}} - r_i)$ are now lower for a given $\theta_o^i$ than were observed at 400 K. Hence, the difference in the initial and maximum reaction rates at
fixed $\theta_0$ do not decrease monotonically with surface temperature as predicted by the simple CO adsorption model given in Equation 4-2.

This observation indicates that other factors influence the reaction rate at early times. One key difference is that the desorption rate of chemisorbed CO molecules, in addition to that of the weakly bound precursors, is significantly higher at 500 K than at the lower temperatures investigated. Consequently, much lower CO surface coverages are obtained at 500 K and the overall CO$_2$ production rate becomes limited by the rate of CO adsorption. This has been shown to be the case by Zaera et al. [21] for CO oxidation at $T_s > 400$ K and $\theta_0 < 0.25$ ML. Although the CO coverages are much lower, the overall CO$_2$ production rate is greater at $T_s = 500$ K than at lower surface temperature. Again, this is evident from the rate curves since the rate maxima are higher at 500 K than at lower temperatures, and the reaction is completed at lower total CO exposures.

4.3.3 Carbon Monoxide Oxidation from Platinum Oxide

The reactivity of CO toward platinum oxide grown on Pt(111) was also investigated using direct rate measurements. Rate curves for CO$_2$ production as a function of the CO exposure are shown in Figure 4-7 for measurements conducted at surface temperatures from 400 to 550 K and with an initial atomic oxygen coverage of 1.7 ML generated using the atomic oxygen beam. At $\theta_0 = 1.7$ ML, the surface is covered with islands or particles of Pt oxide surrounded by domains of chemisorbed oxygen atoms. In each measurement, the CO$_2$ production rate increases abruptly upon initiating the CO exposure, and then rises more slowly to a local maximum followed by decay. The behavior observed at early times is attributed to CO reacting with chemisorbed O-atoms on the unoxidized portions of the surface. This conclusion was verified by
performing similar experiments in which only about half of the sample was located in line-of-sight of the atomic oxygen beam during oxidation of the surface, which resulted in a larger fraction of the surface being covered by chemisorbed O-atoms, rather than oxide, and an increase in the initial feature in the CO₂ production rate curve.

After passing through the first maximum, the CO₂ production rate begins increasing again and gradually reaches a second, higher maximum at CO exposures greater than 20 ML. The rate maximum shifts to longer exposures as the surface temperature is increased from 400 to 550 K. Interestingly, the delay before the rate maximum is significantly longer at Tₛ = 550 K compared with the lower temperatures. However, once the rate begins increasing, the CO exposure required to reach the second maximum is relatively insensitive to the surface temperature. The value of the maximum CO₂ production rate does not differ significantly with surface temperature, nor does it exhibit an obvious trend. The observed variations in the delay before the maximum rate may be caused by differences in the incident CO fluxes that were employed in the measurements. Finally, TPD measurements showed neither the desorption of O₂ nor CO₂ after completion of the isothermal CO oxidation experiments, indicating that all of the oxygen atoms are converted to CO₂ during the beam experiments. It should also be noted that CO₂ evolution was not observed when exposing the oxidized surface to the CO beam at Tₛ = 300 K.

The CO oxidation kinetics observed on the oxidized Pt(111) surface is similar to that reported previously for CO oxidation on high-coverage oxygen phases adsorbed on Pd(100) [107]. In that study, STM images provide evidence that CO oxidation actually occurs on the low-coverage (2x2) phase, but that the high-coverage phases rapidly supply
oxygen to the low-coverage phase. As a result, the (2x2) domains grow on the surface as the high-coverage domains shrink. Although this behavior suggests that the high-coverage phases are more active toward CO oxidation, the weak binding of CO on the high-coverage phases prevents CO from adsorbing on these phases and gives rise to the delay in the overall rate of CO oxidation. A similar mechanism is likely to dictate the oxidation kinetics on oxidized Pt(111).

Figure 4-8 shows the CO$_2$ formation rate as a function of CO exposure measured at a surface temperature of 400 K and for initial atomic oxygen coverages of 1.7, 2.3, and 2.6 ML. As $\theta_0^i$ increases, the time delay prior to the CO$_2$ rate maximum grows longer, and the rate feature also broadens. The maximum reaction rate is also relatively insensitive to the initial atomic oxygen coverage for $\theta_0^i$ from 1.7 to 2.6 ML, and, in fact, is nearly the same magnitude for these initial coverages and incident CO fluxes. An increase in the induction period as well as the rate broadening with increasing $\theta_0^i$ were also observed by Zheng and Altman for CO oxidation on Pd(100) and is therefore consistent with the reaction mechanism proposed by those authors [107]. As the initial oxygen coverage increases in the range where Pt oxide forms, the fraction of the surface on which CO can adsorb decreases, causing a longer delay before reaction initiates. Once the reaction initiates, the reaction rate increases since the area of surface available for CO to adsorb and react increases as the oxide particles are consumed. This mechanism as it applies to CO oxidation on oxidized Pt(111) will be elaborated in Section 4.4.

To probe the distribution of oxygen phases on Pt(111) during the course of the reaction, the CO beam exposure was terminated before and shortly after the CO$_2$ production rate maximum and O$_2$ TPD spectra were collected. Starting with $\theta_0^i = 1.7$ ML,
reaction was carried out at $T_s = 500$ K until the CO exposure reached ~5 ML, which is
during the second induction period (Figure 4-7). The subsequent O$_2$ TPD trace is very
similar to that obtained from the surface before reaction, and indeed we find from
integrating the desorption spectra that less than 5% of the initial oxygen atoms are
removed during the initial 5 ML CO exposure to the surface, and is within the
experimental uncertainty.

Figure 4-9 shows the O$_2$ TPD spectrum obtained after exposing the surface to ~20
ML of CO, which is sufficient to pass the maximum in the CO$_2$ production rate (Fig. 4-
7). The atomic oxygen coverage remaining on the surface is 0.47 ML after the 20 ML
CO exposure. Also shown in the figure are O$_2$ TPD spectra obtained after adsorbing 0.59
and 1.7 ML of oxygen atoms using the atomic oxygen beam with the surface held at 450
K. A rather sharp O$_2$ desorption feature at about 660 K is observed after the long CO
exposure, which is consistent with the majority of surface oxygen atoms residing in oxide
domains. Interestingly, the trailing edge of the desorption feature (~ 750 to 800 K) is
lower than that obtained from the surfaces with initial O-atom coverages of 0.59 and 1.7
ML prepared by O-atom adsorption. Indeed, the trailing edges nearly overlap in the O$_2$
TPD spectra obtained from Pt(111) after adsorbing greater than 0.25 ML of atomic
oxygen (see Figures 4-1 and 4-9). Notice also that the leading edge of the desorption
trace obtained after CO oxidation also lies below the leading edge obtained from the
surface with $\theta_o^i = 1.7$ ML, whereas the opposite behavior is observed when an atomic
oxygen coverage of 0.59 ML is obtained by oxygen adsorption. Thus, as discussed in
Section 4.3.1, the distribution of oxygen phases on the surface depends quite sensitively
on how the oxygen coverage is generated.
Dramatic evidence for the dependence of the oxygen phase distribution on the sample history may be seen in the TPD spectra obtained from Pt(111) covered with 0.47 ML of O-atoms, generated by removal of oxygen atoms from the surface with $\theta_o^i = 1.7$ ML versus O-atom adsorption (Figure 4-9). As shown originally by Koel and coworkers [51,52,55], oxygen atoms populate chemisorbed states at $\theta_o \sim 0.50$ ML when the coverage is reached by the adsorption of active oxidants. At this coverage, the surface is believed to be covered by disordered and ordered domains of chemisorbed oxygen atoms, which give rise to the $\alpha$ and $\beta$ desorption features discussed in Section 4.3.1 and shown in Figures 4-1 and 4-9. The TPD results therefore firstly indicate that oxide domains remain on the surface when the coverage is decreased to at least 0.50 ML by reaction with CO at $T_s = 500$ K. The lower leading and trailing edges of the desorption trace, compared with those obtained after adsorbing O-atoms, indicates further that chemisorbed O-atoms are more reactive toward CO than the oxide phase. Hence, the picture that emerges is that CO adsorbs and reacts selectively on surface domains containing chemisorbed O-atoms. Since CO adsorption on the oxide particles is inefficient, at best, the oxide particles decompose by supplying oxygen to the regions of the surface covered by chemisorbed oxygen atoms where reaction with CO is relatively rapid. The migration of oxygen atoms from the oxide to the low-coverage domains appears to be slow at 500 K, with the result being that most of the surface oxygen atoms remain in oxide domains at about 0.50 ML.

4.3.4 Low Energy Electron Diffraction Results

Forming platinum oxide by exposing Pt(111) to an oxygen atom beam disrupts the long range order of the surface. A series of LEED experiments were performed to
determine qualitatively how the structure of the oxidized Pt(111) surface changes during reaction with CO. At each step, a digital photograph was taken of the LEED image. Before initiating the CO reaction, the surface was initially covered with 1.7 ML of O-atoms by exposing the surface to the oxygen atom beam while holding the surface temperature at 450 K. In this coverage regime, TPD shows that the majority of the oxygen atoms have agglomerated into oxide islands. A LEED image was taken from this surface and is shown in Figure 4-10A. The surface was then exposed to the CO beam with the surface held at 400 K, until CO had removed all of the oxygen from the surface. A LEED image was taken from this surface and is shown in Figure 4-10B. The reduced surface was then flashed to 600 K and 950 K and LEED images were recorded as shown in Figures 4-10C and D respectively.

The diffuse substrate (1x1) pattern, along with a high intensity background may be seen in the LEED image obtained from the oxidized surface (Figure 4-10A), and reveals that oxide island formation roughens the surface significantly. After completely reducing the surface with CO at \( T_s = 400 \) K, the (1x1) pattern of the Pt(111) substrate sharpens and the diffuse background diminishes significantly (Figure 4-10B), indicating that the removal of oxygen by CO restores the long-order of the surface considerably, even at \( T_s \) as low as 400 K. The faint background that may be seen in the LEED image could arise from small quantities of CO remaining on the surface after reaction, or may indicate that the long-range order of the surface was not restored to its condition before oxidation. Heating the surface to 600 K desorbs all of the CO from the surface, but does not noticeably reduce the background intensity in the LEED image (Figure 4-10C), thereby suggesting that the Pt surface does maintain a degree of disorder after the removal of
oxygen by CO at 400 K. Heating the surface to 950 K causes the diffuse background to diminish (Figure 4-10D), indicating that elevated temperatures are required to improve the crystallinity of the surface after oxidation and then reduction by CO.

4.4 Discussion

The isothermal CO oxidation experiments conducted with $\theta_O < 0.5$ ML, at each temperature show that the CO$_2$ formation rate is characterized by an initial jump, which proceeded through a rate maximum, and finally decayed back to the baseline. The reaction rates increased with surface temperature, indicating that an increase in the rate constant compensates for the decrease in $\theta_{CO}$ with increasing temperature. Qualitative features such as the $\theta_O$ dependent variations in the quantity $(r_{\text{max}}^i - r_{\text{i}})$ were captured quite well by the precursor mechanism described by Piccolo et al. [106]. However, this model does not capture all of the physics, one such example being the non-monotonic variation of the quantity $(r_{\text{max}}^i - r_{\text{i}})$ with $T_s$.

Possible differences between our reaction system and the model, given by Equation 4-2, may be responsible for these discrepancies. For example, the model assumes that $\theta_{CO_{\text{sat}}}$ remains constant. The TPR data obtained in the present study shows that the maximum amount of CO deposited on the surface remains constant for $\theta_O$ in the range of 0.25-0.6 ML. However, $\theta_{CO_{\text{sat}}}$ varies significantly below a 0.25 ML coverage of adsorbed oxygen atoms.

Additionally, an implicit assumption of model is an average $\theta_O$ dependence on the CO sticking probability. Temperature programmed desorption shows three distinct desorption features in this coverage range. Temperature programmed reaction conducted after saturating CO on the high coverage phases of oxygen revealed a reduction in all
three oxygen desorption states. This indicates that multiple oxygen phases reside on the surface and react with CO. It is possible that the CO sticking probability may be different on each phase.

Finally, the activation energy for desorption of oxygen is different in each state. Temperature programmed reaction measurements show that the CO will preferentially react with oxygen atoms in the $\alpha$ state. This strongly implies that the rate constant for the CO oxidation reaction may be dependent on $\theta_0$. Despite the rich CO and O-atom behavior on Pt(111), the model given by Piccolo et al. [106] does reproduce the main kinetic features of this system quite well in the oxygen atom coverage range of 0.25-0.6 ML.

Carbon monoxide oxidation on platinum oxide follows a reaction kinetic behavior that differs from that observed for high coverage phases of chemisorbed oxygen atoms on Pt(111). Indeed, the CO oxidation kinetics appears similar to that observed on palladium surfaces covered with high density oxygen phases [106,108-110]. Of particular relevance is an investigation performed by Zheng and Altman [107], where they studied the reactivity of various oxygen phases on Pd(100) toward CO. Surfaces with different atomic oxygen phases were exposed to CO while monitoring the partial pressure of CO$_2$. As the atomic oxygen coverage increased, the delay before the onset of CO$_2$ formation increased and the CO$_2$ reaction feature broadened.

The temperature dependence of the rate behavior was explained through a limited lifetime of a precursor CO molecule on the surface. As the surface temperature increases, the CO lifetime on the surface decreases, reducing the reaction rate. The relative reactivity of carbon monoxide was highest on the lowest oxygen coverage phase, and
decreased as the O-atom density increased. This decrease in the reaction rate with increasing oxygen coverage was explained by a decrease in the CO sticking probability on the high density O-atom phases. To explain their rate curves, they propose that there is a rapid exchange between these phases, with the oxide (surface or bulk) rapidly supplying O-atoms to the lower coverage phases, which is then consumed in the CO oxidation reaction. Thus, the phase with the highest O-atom density feeds the phase with the next highest O-atom density. This was confirmed by STM measurements, which show that only areas diminished during the reaction was the portion covered by the highest O-atom density phase. Once the highest density phase was removed, the surface area covered by the phase with the next highest density began to shrink. As these phases are removed, domains form on which CO has a higher sticking probability, thereby promoting the CO oxidation reaction.

The CO oxidation rate behavior observed by Zheng et al. appears very similar to the rate curves obtained from the oxidized Pt(111) surface. Specifically, they observed a delay before the reaction initiated, followed by a gradual rise toward the rate maximum. In our study, we observed a delay before the rate initiation, which is attributed to a low sticking probability of CO onto the oxidized surface. Additional supporting evidence for this is given in the Section 4.3.1, where CO was found not to appreciably adsorb onto the oxide even at 100 K.

Zheng et al. observed a rapid equilibrium between the oxygen phases on Pd(100). In our study, the equilibrium between the phases with different O-atom density does not appear to be rapid. First, consider the TPR results. The $\gamma$ desorption state correspond to chemisorbed oxygen atoms with the highest surface-binding energy. After TPR was
conducted with 0.59 ML of O-atoms and about 0.30 ML of CO molecules, a decrease in the quantity of oxygen desorbing the $\gamma$ feature was observed. This suggests firstly that some oxygen atoms in the $\gamma$ state are converted to CO$_2$ and secondly that the migration of oxygen atoms into these states is slow. Also the TPD spectrum taken after partially reducing the oxidized surface with CO shows that oxygen residing on the surface exists primarily as oxide islands. Further evidence for the slow process comes from contrasting the rate data with $0 < \theta_o^i < 0.5$ ML with that of the oxide. The reaction rate increased with temperature for the O-atom covered surface, whereas the overall reaction rate appears to remain independent of temperature for reaction with the oxide. This suggests that the oxide does not efficiently supply the adatom phase with O-atoms, limiting the reaction region to the interface between the platinum metal and the oxide interface. Since this process is slow, it is assumed to be rate limiting.

The slow initial CO oxidation rates from the oxidized surface can be interpreted as CO reacting at the island interfaces. Once metallic domains are nucleated, the oxide slowly supplies oxygen to the reaction at the metal sites near the island boundaries. Additional supporting evidence comes from the CO oxidation curves with increasing amounts of oxide initially deposited on the surface. As the oxide coverage increases, a corresponding increase was observed in the lag before the onset of CO$_2$ formation. This is consistent with the idea that the reaction with the oxide occurs primarily at island boundaries, where the quantity of platinum metal sites decreases as the oxide grows.

4.5 Conclusions

Carbon monoxide oxidation was investigated on Pt(111) surfaces with initial oxygen coverages greater than 0.25 ML. At 100 K, CO was not observed to adsorb onto
platinum oxide. However, CO readily adsorbed onto Pt(111) with a surface concentration of oxygen atoms in the range of 0.25-0.6 ML, with the saturation CO coverage remaining constant at about 0.30 ML. Temperature programmed reaction from these surfaces showed the formation of carbon dioxide as well as desorbing carbon monoxide and oxygen. An examination of the O$_2$ desorption features clearly shows a preference for CO reaction with oxygen atoms that generate the $\alpha$ desorption state and that the oxygen migration between the desorption states is slow.

The isothermal reaction data shows that the reaction kinetics for CO oxidation platinum oxide differs significantly from that observed for chemisorbed O-atoms on Pt(111). High coverage oxygen phases (0.25-0.6 ML) reacting with CO were studied as a function of surface temperature, and the reaction kinetics closely follows a precursor-mediated mechanism for CO adsorption. Similar studies were performed on platinum oxide, and each curve has the following characteristics. A delay is observed before the onset of the reaction, followed by an increase in the reaction rate towards the maximum and a subsequent decay to the baseline. This indicates that the oxidation reaction occurs primarily at the interface between the oxide and the metal surface. The reaction rate initiation was most efficient at the lowest temperature examined, and is attributed to longer CO precursor lifetimes on the surface.

A large amount of disorder is observed upon oxidizing Pt(111). LEED results show a restoration of the (1x1) pattern with the presence of a background when reducing the surface with CO at 400 K, indicating a significant amount of order regeneration. The background was only removed after flashing the sample to annealing temperatures. This
shows that the surface order is not completely restored by reducing the surface with CO at 400 K.

Table 4-1. Maximum CO coverage achieved as a function of initial $\theta_O$

<table>
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<th>Initial $\theta_O$</th>
<th>Total $\theta_{CO}$</th>
<th>$\theta_O$ desorbing</th>
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<td>0.00</td>
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Figure 4-1. Temperature programmed desorption spectra taken from the Pt(111) surface with a ramp rate of 3 K/sec. Left panel: coated with 0.25, 0.39 and 0.59 ML oxygen atoms. Three desorption states are observed and labeled $\alpha$, $\beta$ and $\gamma$. Right panel: TPD spectra taken from an oxidized Pt(111) surface with a coverage of equal to 1.7 ML compared with TPD taken with a coverage of 0.25 ML.
Figure 4-2. Temperature programmed reaction spectra taken with a ramp rate of 1 K/sec, showing O₂, CO and CO₂ desorption after preparing a saturation coverage of CO on Pt(111) with 0.39 ML of O-atoms at Tₛ = 100 K.
Figure 4-3. Temperature programmed desorption and reaction spectra taken from the Pt(111) surface with a ramp rate of 3 K/sec. Left Panel: An oxygen TPD spectrum from Pt(111) with an oxygen atom coverage of 0.59 ML compared with a TPR spectrum taken when this surface was saturated with CO. Right panel: A TPR spectrum yielding an oxygen atom coverage of 0.33 ML compared with a TPD spectrum corresponding to a 0.25 ML coverage of O-atoms on Pt(111).
Figure 4-4. Left panel: Carbon dioxide pressure traces with initial oxygen coverages of 0.25 ML ($\phi_{CO} = 0.12$ ML/sec), 0.33 ML ($\phi_{CO} = 0.09$ ML/sec) and 0.44 ML ($\phi_{CO} = 0.10$ ML/sec) taken while the Pt(111) sample was held at 300 K plotted against CO exposure. Right panel: Calculated rate of CO$_2$ formation plotted as a function of $\theta_O$. 
Figure 4-5. Left panel: Carbon dioxide pressure traces with initial oxygen coverages of 0.25 ($\phi_{\text{CO}} = 0.12 \text{ ML/sec}$), 0.37 ($\phi_{\text{CO}} = 0.09 \text{ ML/sec}$) and 0.45 ML ($\phi_{\text{CO}} = 0.10 \text{ ML/sec}$) taken while the sample was held at 400 K, plotted against CO exposure. Right panel: Calculated rate of CO$_2$ formation plotted as a function of $\theta_0$. 
Figure 4-6. Left panel: Carbon dioxide pressure traces with initial oxygen coverages of 0.25 ML ($\phi_{CO} = 0.12$ ML/sec), 0.35 ML ($\phi_{CO} = 0.10$ ML/sec) and 0.48 ML ($\phi_{CO} = 0.11$ ML/sec) taken while the Pt(111) sample was held at 500 K, plotted against CO exposure. Right panel: Calculated rate of CO$_2$ formation plotted as a function of $\theta_O$. 
Figure 4-7. Carbon dioxide formation rate plotted as a function of CO exposure with an initial O-atom coverage of 1.7 ML at surface temperatures of 400 ($\phi_{\text{CO}} = 0.11$ ML/sec), 450 ($\phi_{\text{CO}} = 0.09$ ML/sec), 500 ($\phi_{\text{CO}} = 0.12$ ML/sec) and 550 K ($\phi_{\text{CO}} = 0.10$ ML/sec).
Figure 4-8. Carbon dioxide formation rate plotted as a function of CO exposure with initial O-atom coverages of 1.7, 2.3 and 2.6 ML with surface temperature held constant at 400 K.
Figure 4-9. TPD traces taken with an initial coverage of 1.7 ML and with the same coverage after a 20 ML CO exposure (0.47 ML) at 500 K. The dashed trace corresponds to a surface with an initial O-atom coverage of about 0.5 ML.
Figure 4-10. LEED images taken with an electron energy of 163 eV, $L_{1/3} = 518$ V, $L_2 = 32$ V, Screen = 4 kV, Wehnelt = 0, and suppressor = 9V on A) Pt(111) covered with 1.7 ML of oxygen atoms, B) after removing all of the oxygen from part a with CO at 400 K, C) flashing the sample prepared in B to 600 K to remove all adsorbed CO, and D) flashing the surface to 950 K. Each image has been inverted and the contrast has been slightly changed by the same amount to enhance the background.
CHAPTER 5
CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.1 Synopsis

Investigations of the interactions of oxygen atoms with solid surfaces provided deeper insight into semiconductor oxidation. By performing XPS before and after exposing nitrided Si(100) to a plasma activated O$_2$ beam, conclusive evidence was found showing that the oxygen atoms primarily adsorb at dangling bond sites with a negligible amount of direct insertion into silicon-silicon bonds. The primary reason that silicon nitride is resistant to oxidation is its lower dangling bond density compared with pure Si surfaces. Through quantitative analysis of the N1s and O1s spectra, it was determined that the nitrogen species remained phase separated from the oxidic phase.

Molecular oxygen is known to chemisorb onto Pt(111) at cryogenic temperatures. Exposure of adsorbed $^{18}$O$_2$ to gaseous $^{16}$O-atoms yields both displacement and dissociation of $^{18}$O$_2$ initially adsorbed on Pt(111). The desorption rate increased with surface temperature, whereas the desorption yield decreased with surface temperature. Upon performing TPD, it was determined that the balance of $^{18}$O$_2$ dissociated on the surface. The initial displacement probabilities (displacement rate/$^{16}$O-atom impingement rate) are 0.48, 0.50 and 0.54 at 90, 100 and 110 K, respectively. Dissociation occurred only during the first 40 seconds (0.2 ML fluence of $^{16}$O-atoms) of the exposure and the initial dissociation probabilities (dissociation rate/$^{16}$O-atom impingement) are estimated to be 0.3, 0.48 and 0.66 at 90, 100 and 110 K, respectively. An apparent average activation energy of $\sim$3 kJ/mol was found for dissociation, which can be easily
surmounted by the energy dissipated as the $^{16}\text{O}$-atoms adsorb onto Pt(111) (350 kJ/mol). The temperature dependence of the dissociation probability, and the low activation energy for dissociation were interpreted as evidence of an increasing peroxo population with surface temperature, with the peroxo species more susceptible to dissociate.

By exposing platinum surfaces to active oxidants such as atomic oxygen, high oxygen coverages on Pt(111) can now be prepared under UHV conditions. This provides the means to conduct molecular beam studies on this important catalyst. The reactivity of high oxygen coverage phases generated on Pt(111) toward CO oxidation was probed through isothermal kinetic measurements, TPD, TPR, and LEED. CO uptake in the O-atom coverage range of 0.25 to 0.6 ML was independent of O-atom coverage. However, no CO uptake was observed on platinum oxide. The oxygen atoms with the lowest surface binding energy preferentially reacted to form CO$_2$. High coverage oxygen phases (0.25-0.6 ML) reacting with CO were studied as a function of surface temperature, and the reaction kinetics closely follows a precursor-mediated mechanism for CO adsorption. CO oxidation on platinum oxide occurs at the interface between the metallic regions and the oxide islands. LEED results show a significant amount of order restoration when reducing the oxidized surface with CO at 400 K. The presence of a background indicates that some degree of disorder remains on the surface at 400 K.

5.2 Future Work

5.2.1 Nonthermal Reaction Mechanisms

The ability to generate gas phase atomic oxygen presents an opportunity to contribute in the areas of space vehicle degradation, plasma processing, plasma catalysis, combustion reactions, and fundamental reaction mechanisms. A means of contributing to each area would be to perform molecular level studies on these systems. Experiments
can be designed to investigate these systems by preparing well defined surface-adsorbate systems and subsequently exposing these surfaces to the O-atom beam. One could then tailor the materials in these volatile reaction environments to achieve the desired results.

5.2.2 Scanning Tunneling Microscopy Measurements

LEED images have provided some information regarding surface structural changes during the oxidation of Pt(111). Particularly relevant data regarding the long range order of the surface was obtained on the O-atom/Pt(111) system. More detailed information can be obtained using the atomic resolution capabilities of STM. This would serve to verify the information obtained through the LEED measurements, and also determine the structural characteristics of the oxide islands.

Scanning tunneling microscopy would also provide valuable information as the adsorbed oxygen species reacts with CO. The kinetic data and TPR measurements suggest an inhomogeneous O-atom removal mechanism during the course of the reaction. Using STM, it would be possible to determine the structures of the oxygen phases as they are removed during the reaction. This would provide deeper insight into the surface sites that are reactive toward CO oxidation.

5.2.3 Mechanistic Catalytic Studies

Catalytically active metal oxides can now be formed under UHV conditions, by exposing metallic surfaces to an active oxidant such as O-atoms. This enables molecular level surface induced reactions to be studied on these new oxygen phases on Pt(111). Immediate suggestions for future studies would be to grow platinum oxide on Pt(111) and conduct reactive scattering measurements with relevant reagents in the molecular beam such as hydrocarbons or NOx gases.
Alternatively, similar experiments can be performed on different platinum crystal faces. This would provide another dimension in these reaction studies revealing both how the oxide structure varies on these faces, and the reactivity of these different oxide structures towards the reactant in question. A comparison of this data would contribute to the structural design of model catalysts, which would better simulate actual reactive surface particles.

These experiments by no means should be limited to platinum. Several catalytically active metals such as palladium, gold, iridium, and ruthenium should be examined in this manner as well. As a detailed understanding of the reactions on these surfaces and oxides are developed at the molecular level, improved catalytic materials and processes can be engineered.
LIST OF REFERENCES


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BIOGRAPHICAL SKETCH

Alex Gerrard was born on February 27, 1977 in Portsmouth, NH to Alex and Mary Gerrard. When he was 4 years old, his father was assigned to work at Elmendorf Air Force Base in Anchorage, AK. This is where Alex grew into adulthood with his brother Aaron and two sisters Anne and Allanah. While attending Service High School, Alex had the opportunity to participate as a foreign exchange student to Magadan, Russia and Shari-cho, Japan.

His college level studies began after graduating from high school in May 1995. In May 1999, he earned a B.S. degree in Chemical Engineering from the University of Missouri-Rolla. Alex enrolled in the Ph.D. program at the University of Florida in August 1999, where he joined Assistant Professor Jason Weaver’s group. As one of Dr. Weaver’s first students, Alex’s first task was to set up a Surface Science laboratory in which to conduct his research.

Along with his academic studies, Alex has spent a great deal of time working on self development and studying human interactions. These studies have comprised of abstract areas such as theology and philosophy to practical subjects including leadership and conflict resolution. One of Alex’s strongest personal convictions is to support the community. While residing in Gainesville, he has volunteered his time visiting the elderly at nursing homes and assisted at a local church. In his spare time, Alex enjoys spending his time traveling, reading, and baking.