Atomic Oxygen Adsorption and Absorption on RH(111) and AG(111)

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ATOMIC OXYGEN ADSORPTION AND ABSORPTION ON RH(111) AND AG(111)

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Once in a while you get shown the light
In the strangest of places if you look at it right

Robert Hunter/Grateful Dead, *Scarlet Begonias*
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<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AO</td>
<td>Atomic oxygen</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CMA</td>
<td>Cylindrical mirror analyzer</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>FCC</td>
<td>Face-centered cubic</td>
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<tr>
<td>HCC</td>
<td>Hexagonal close packed</td>
</tr>
<tr>
<td>Ir</td>
<td>Iridium</td>
</tr>
<tr>
<td>$I_t$</td>
<td>Tunneling current</td>
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<tr>
<td>LDOS</td>
<td>Local density of states</td>
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<tr>
<td>LEED</td>
<td>Low energy electron diffraction</td>
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<tr>
<td>LEEM</td>
<td>Low energy electron microscopy</td>
</tr>
<tr>
<td>LN$_2$</td>
<td>Liquid nitrogen</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>Nitrogen dioxide</td>
</tr>
<tr>
<td>O$_{ad}$</td>
<td>Adsorbed oxygen</td>
</tr>
<tr>
<td>O$_{sub}$</td>
<td>Subsurface oxygen</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>Rh</td>
<td>Rh</td>
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<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>Ta</td>
<td>Tantalum</td>
</tr>
<tr>
<td>$T_{fil}$</td>
<td>Filament temperature</td>
</tr>
<tr>
<td>$T_{max}$</td>
<td>Temperature at maximum desorption</td>
</tr>
<tr>
<td>$T_{sam}$</td>
<td>Sample temperature</td>
</tr>
<tr>
<td>TMP</td>
<td>Turbomolecular pump</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high vacuum</td>
</tr>
<tr>
<td>$V_b$</td>
<td>Tunneling bias</td>
</tr>
<tr>
<td>W</td>
<td>Tungsten</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Work function</td>
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<tr>
<td>$\theta_O$</td>
<td>Oxygen coverage</td>
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ABSTRACT

A central question in the field of heterogeneous catalysis is how surface structure and subsurface species influence catalytic behavior. One key to answering that question is determining which surface structures and subsurface species are present under catalytically relevant conditions. This dissertation presents results of Auger electron spectroscopy, low energy electron diffraction, temperature programmed desorption, and scanning tunneling microscopy experiments on oxidized Rh(111) and Ag(111) crystals. Exposing Rh(111) to O$_2$ produced a predominately (2 × 1) adlayer, but even after extended dosing, (2 × 2) domains were also present. Exposing Rh(111) to atomic oxygen yielded O coverages greater than 0.5 ML and (1 × 1) domains were observed to form along terrace step edges. However, (2 × 1) and (2 × 2) domains were still present.

Atomic oxygen was used to oxidize Ag(111) in order to study the effect of sample temperature as well as oxygen flux and energy. When atomic oxygen was generated using a lower temperature thermal cracker, a variety of previously reported surface structures were observed. When O was generated using a higher filament temperature, the surface became highly corrugated, layers of Ag$_2$O appeared to form, and little subsurface oxygen was observed. To investigate the role of sample temperature, the Ag(111) sample was held at various temperatures while being exposed to atomic oxygen. For short doses, sample temperature had minimal effect on surface reconstruction. For longer doses, changes in sample temperature in the range of 490 K to 525 K had a substantial impact.
on surface reconstruction and subsurface oxygen absorption. Higher temperature dosing yielded the same surface structures which were observed after short doses. Lower temperature dosing with atomic oxygen resulted in subsurface oxygen formation and new structures which covered the surface. The results indicate the rich complexity of oxygen/transition metal interactions and illustrate how reactive species can be used to produce high coverage surface structures under UHV conditions.
CHAPTER ONE
INTRODUCTION

Heterogeneous catalysis impacts modern life in a multitude of ways. Catalytic reactions are involved in over 90% of chemical manufacturing processes and contribute to approximately 35% of the world’s GDP. Heterogeneous catalysts are also involved in energy applications ranging from oil refining to fuel cells, environmental applications including mitigating automobile emissions and groundwater purification, medical application such as pharmaceutical production and biosensors, and food production through the synthesis of fertilizers and pesticides. A central question facing the field of heterogeneous catalysis is how surface structure and subsurface species determine chemical behavior. Within surface science, there have been significant efforts made to fully characterize carefully prepared metal surfaces, and then use these as models to elucidate the chemistry takes place under actual catalytic conditions. Similarly, identification of a particular surface structure has often been used to indicate what chemically active species are present, and therefore, what reactions one would expect to take place on such a surface.

Most important heterogeneously catalyzed reactions require high temperatures and pressures to surmount sizable activation barriers and to provide sufficient numbers of collisions to realize significant turnover. At high temperatures and pressures, the surfaces of catalytically active transition metals have been shown to be dynamic. For
many late transition metals, in addition to adsorbate induced surface structures and reconstructions, a variety of high coverage bulk and two dimensional oxide structures can also be formed under catalytic conditions. Research suggests that in some cases these oxide phases, rather than the bare metal surface, might be the active phases for catalysis. For other cases, formation of oxide layers may deactivate or poison catalysts. In order to develop accurate, predictive models of heterogeneously catalyzed reactions, a detailed understanding of high coverage oxide structures representative of actual catalytic surfaces under catalytic conditions is necessary.

A key challenge to using traditional surface science methods to study heterogeneous catalysts has been described as a pressure gap. The gap results from the fact that the ultra-high vacuum (UHV) conditions which are necessary, or at least advantageous, for many surface science methods frequently inhibit the formation of catalytically relevant surface structures. Simply put, structures formed under pristine vacuum conditions are often quite different than structures formed when the pressure is a billion or more times greater. One approach to the pressure gap problem is to adapt and improve surface science methods so that they work at elevated pressures. Significant progress has been made with this approach, particularly with X-ray photoelectron spectroscopy and scanning tunneling microscopy.

While advancements in ambient and in situ surface science techniques have provided insight toward the development of our understanding of catalytic surfaces under reaction conditions, the need remains for high-precision UHV studies that provide atomic level information. The details obtainable under UHV conditions, particularly when combined with the information learned from elevated pressure studies, can provide the
basis for predictive models of heterogeneously catalyzed reactions. A second approach to the pressure gap problem that still utilizes UHV surface science methods is to use highly reactive species to reproduce high coverage structures under UHV conditions. This approach was followed for the research for this dissertation. Atomic oxygen and NO\textsubscript{2} were used to oxidize two important transition metal catalysts, Rh and Ag, under a variety of conditions. After dosing, the samples were studied using conventional UHV methods including STM, Low energy electron diffraction, (LEED), Auger electron spectroscopy (AES), and temperature programmed desorption (TPD).

**Rhodium**

Rhodium is one of the rarest and most expensive metals. Due to its high cost and limited malleability, the use of Rh is limited mainly to catalysis. As a catalyst, Rh is used in a wide variety of processes including petroleum refining, ethanol steam reforming, hydrogenation, CO oxidation, and NO\textsubscript{x} reduction. The most significant use of Rh is for NO\textsubscript{x} reduction in automobile catalytic converters. In 2012, approximately 80% of the 30,000 kg of Rh consumed worldwide was used in three-way automobile catalytic converters.

![Figure 1. Rhodium crystal structure. (L) Face-centered cubic structure. (R) (111) face with arrows pointing to hcp and fcc surface sites.](image-url)
Rh has a face-centered cubic (fcc) crystal structure, and consequently the (111) face is the most stable and has been the most extensively studied.\textsuperscript{46} Due to role of Rh as a partial oxidation catalyst, a large focus of Rh research has been on the interaction of oxygen with Rh(111) face. The debate over the structures formed by oxygen adsorption on Rh(111) has occasionally been contentious.\textsuperscript{47} Grant and Haas used LEED data to conclude that, at room temperature, O\textsubscript{2} formed an ordered (2 × 2), structure on Rh(111).\textsuperscript{48} Somorjai and co-workers, also using LEED and dosing with O\textsubscript{2} at room temperature, came to the same conclusion in 1978.\textsuperscript{49} Based on TPD data, Somorjai’s group also concluded that O\textsubscript{2} most likely dissociated on the Rh(111) surface and desorbed with second order kinetics. A (2 × 2) structure, shown in Figure 2(A), has an oxygen surface coverage (θ\textsubscript{O}) of 0.25 ML. Thiel and co-workers found that O\textsubscript{2} adsorption was disordered at 100 K, but that an ordered (2 × 2) structure formed when the sample was heated >150 K.\textsuperscript{50} In 1980, Somorjai’s group reinterpreted their results and found that the apparent (2 × 2) LEED pattern was instead due to a (2 × 1) structure with θ\textsubscript{O} = 0.5 ML.\textsuperscript{51} A tensor LEED analysis by Mitchell’s group supported Somorjai’s conclusion. They found that the LEED pattern from a (2 × 2) structure would be difficult to distinguish from the pattern of three (2 × 1) domains, each rotated by 60°. They concluded that a (2 × 1) surface structure with O atoms in fcc sites was more likely than a (2 × 2) structure.\textsuperscript{52} XPS and He diffraction studies from other authors provided additional support for the (2 × 1) structure at saturation.\textsuperscript{53,54}
Xu and Ng subsequently published a paper arguing that the original interpretation that, at room temperature, oxygen saturates at 0.25 ML in a (2 × 2) structure on Rh(111) was correct.\textsuperscript{55} In addition to LEED and AES, their study utilized STM imaging. However, Xu and Ng’s findings were strongly challenged by other authors.\textsuperscript{56} In 2005, Wintterlin’s group published STM results which showed three (2 × 1) domains rotated by 60° from each other.\textsuperscript{47} Currently, the widely accepted model is that at low coverages O atoms are initially dispersed about the surface. Volatile (2 × 2) islands nucleate with increasing O adsorption and when θ_o reaches 0.25 ML, the (2 × 2) structure is prevalent. As θ_o increases from 0.25 to 0.5 ML, the surface again appears disordered as the (2 × 2) domains are converted into (2 × 1) structures by the insertion of O_{ad} into the (2 × 2) cells.
As $\theta_O$ nears 0.5 ML, the surface consists of domains of $(2 \times 1)$, oriented along one of three axes differing by $60^\circ$.\textsuperscript{47}

Although dosing Rh(111) with O$_2$ under UHV conditions results in a maximum $\theta_O$ of 0.5 ML, higher oxygen coverages have been observed. Computational studies by two groups in the late 1990s concluded that a $(1 \times 1)$ structure would be stable on Rh(111).\textsuperscript{57,58} The limitation on oxygen coverage was believed to be kinetic rather than thermodynamic. Oxygen preferentially binds to fcc surface sites rather than hcp sites which are directly above an atom in layer below the surface.\textsuperscript{59} Although the $(1 \times 1)$ is thermodynamically possible, dissociation of O$_2$ on Rh(111) requires two adjacent fcc sites. Therefore, coverages above 0.5 ML are kinetically unlikely from the dissociation of O$_2$ on the surface.\textsuperscript{60} O$_2$ dosing on Rh(111) was a case where high coverage structures that were potentially important in catalysis had not been observed under UHV conditions.

Oxygen coverages over 0.5 ML were eventually observed by using reactive species such as atomic oxygen and NO$_2$, or much higher O$_2$ pressures.\textsuperscript{61,62,19} Sibener and co-workers were able to achieve a $\theta_O > 1.0$ ML with a beam of AO. Using He diffraction, they identified well-ordered $(1 \times 1)$ surface structures, but TPD experiments showed greater than 1.0 ML of O$_2$ desorption. They concluded that oxygen was absorbed into the bulk, and that the absorption into the bulk was facilitated by the $(1 \times 1)$ surface.\textsuperscript{59}

Varga and co-workers observed $(2\sqrt{3} \times 2\sqrt{3})$R$30^\circ$ and $(2 \times 2)$-3O structures after exposing Rh(111) to $1.3 \times 10^{-3}$ mbar O$_2$ at 400 K for 300 s.\textsuperscript{19} The calculated $\theta_O$ for the two structures was 0.66 and 0.75 ML respectively. Unlike previously observed Rh(111)/O structures in which oxygen adsorbed only to fcc sites, oxygen also adsorbs to hcp sites in the proposed $(2\sqrt{3} \times 2\sqrt{3})$R$30^\circ$ and $(2 \times 2)$-3O structures. The $(2\sqrt{3} \times 2\sqrt{3})$R$30^\circ$, shown in
Figure 2(D) contains 8 oxygen atoms per unit cell, with 6 in fcc sites and 2 in hcp sites. DFT calculations by Varga’s group showed that the structures were less stable than both surface and bulk oxide phases. However, the oxides were kinetically hindered, and only formed at higher pressures or temperature > 800 K.

For this project, both O\textsubscript{2} and AO were used to dose a Rh(111) sample at room temperature.\textsuperscript{63} STM imaging and TPD data showed that at high total coverages of oxygen, (2 × 1), (2 × 2), and (1 × 1) structures coexisted. Using AO generated by thermally cracking O\textsubscript{2}, total oxygen coverages greater than 0.5 ML were readily achieved. STM images showed that well-ordered surface structures remained even at coverages > 1.3 ML. These results show that under room temperature UHV conditions, high coverage surface phases coexist with multiple other phases and that oxygen absorption into the subsurface occurs.

**Silver**

Unlike Rh, Ag is relatively abundant and is one of the least expensive precious metals.\textsuperscript{64} Silver has wide ranging applications including data storage, transparent conducting oxides, and antimicrobial coatings.\textsuperscript{65} Silver is also used as a catalyst for the partial oxidation of many light alkanes.\textsuperscript{66} The two most important reactions catalyzed by Ag are the partial oxidation of methanol and the epoxidation of ethylene.\textsuperscript{67} Methanol oxidation is used industrially to produce formaldehyde, an important industrial intermediate. The process is typically carried out at ≈900 K using a mixture of methanol and air over an unsupported Ag catalyst.\textsuperscript{68} Ethylene epoxidation is used to produce ethylene oxide (EO), an important intermediate in the production of plastics, glycols, and polyesters.\textsuperscript{69} EO is the largest volume industrial product produced by selective
Industrial ethylene epoxidation is carried out under an oxygen atmosphere at 500-600 K over supported Ag catalysts.

Significant surface science studies of the O/Ag system can be traced to the 1970s. Rovida and co-workers first reported a (4 × 4) LEED pattern after dosing Ag(111) with O₂ in the range of 10⁻³ to 1 Torr. The structure, which they attributed to adsorption of O₂ molecules, was stable up to 500-600 K. The same group published another paper two years later replacing the molecular O₂ explanation for the (4 × 4) pattern with the idea of a two dimensional oxide. The change was due to the realization that the unit cell of the Ag₂O (111) face was within 0.3% of four times the Ag(111) unit cell, but they did not provide a detailed structure. Following Rovida, other groups reported the same (4 × 4) LEED pattern, but did not revise the proposed model. Lambert’s group used a variety of surface science methods to look at Ag samples after dosing with high pressure O₂. They observed a (4 × 4) overlayer after dosing Ag(111) at 400–500 K with ≈1 Torr of O₂. A TPD spectra of the overlayer showed a desorption temperature of 580 K.
Campbell also conducted extensive studies of O\textsubscript{2} adsorption on Ag using a variety of surface science techniques.\textsuperscript{77} He calculated that the dissociative sticking probability of O\textsubscript{2} on Ag(111) was approximately $1 \times 10^{-6}$. Consequently, high O\textsubscript{2} pressures were necessary to oxidize the surface. Campbell found that exposing an Ag(111) sample to 5 Torr of O\textsubscript{2} for 20s at 490 K produced a sharp $p(4 \times 4)$ LEED pattern that desorbs at 579 K. Exposing the surface briefly to 1,400 Torr of O\textsubscript{2} at 443 K yielded Ag\textsubscript{2}O bulk oxide. Campbell found that even after heating the $p(4 \times 4)$ structure to partially desorb O\textsubscript{2}, a clear $p(4 \times 4)$ LEED pattern was visible. From that he concluded that the $(4 \times 4)$ structure coalesced into islands. The saturated $(4 \times 4)$ structure was found to have a $\theta_0$ of 0.41 ML(±10%), or 6–7 O atoms per $(4 \times 4)$ cell. This value was very close to the calculated value of 0.375 ML for a single trilayer of Ag\textsubscript{2}O having a layer of Ag atoms between two O layers.\textsuperscript{78}

Although he used high O\textsubscript{2} pressures when dosing Ag(111), Campbell noted that surface carbonate contamination was a potential concern. In order to avoid problems associated with dosing at elevated pressures, Bare et al. used NO\textsubscript{2} to dose Ag(111).\textsuperscript{34} Dosing at 508 K with NO\textsubscript{2} and a microcapillary doser, they were able to form an ordered surface structure while maintaining UHV conditions. LEED and XPS analysis of the surface was consistent with studies using O\textsubscript{2} dosing. TPD spectra taken with a temperature ramp of 5 Ks\textsuperscript{-1} were similar to earlier work, but showed evidence of two overlapping peaks separated by 10 K, rather than a single peak. Bare et al. also calculated that the $\theta_0$ of the $p(4 \times 4)$ structure at saturation was 0.51 ML (±0.04 ML). Analysis of the TPD data showed that approximately 70%, or 0.37 ML, came from the lower temperature peak. As a result, Bare et al. concluded that NO\textsubscript{2} dosing yielded a $p(4 \times 4)$
structure consistent with the Rovida-Campbell model with an additional 0.14 ML of randomly adsorbed O atoms. Raukema and colleagues later reported TPD results similar to Bare’s after dosing with a molecular O\textsubscript{2} beam.\textsuperscript{79} They found that the split of the desorption peak into two peaks was not observable unless the TPD ramp rate was ≤ 10 Ks\textsuperscript{-1}. This explained why Campbell and Rovida et al., who used ramp rates > 10 Ks\textsuperscript{-1}, had only seen a single desorption peak. Unlike Bare et al., the Raukema group found a θ\textsubscript{O} of 0.40 ML (±0.02 ML) for the saturated \(p(4 \times 4)\) structure.

Carlisle and King were the first to use STM to image O/Ag surface structures using the NO\textsubscript{2} dosing procedure developed by Bare et al. Images showed an ordered hexagonal lattice.\textsuperscript{80} Based on the images and STM simulations by the Sautet group, they modified the earlier Rovida-Campbell model of the \(p(4 \times 4)\) structure. The model proposed, shown in Figure 3(R), was similar to the Rovida–Campbell trilayer model, but with some of the overlayer Ag atoms removed. Instead of 2:1, the stoichiometry of the Carlisle model was Ag\textsubscript{1.83}O. Carlisle et al. argued that the hexagonal array in the STM images was due to the Ag atoms remaining in the middle of the Ag/O hexagonal arrays. In an additional study, King’s group was able to form a well-ordered \(p(4 \times 4)\) structure after dosing with NO\textsubscript{2} at 470 K.\textsuperscript{81} Although O\textsubscript{2} desorbs from Ag(111) at ≈580 K, they found significant changes in the surface after annealing the \(p(4 \times 4)\) structure at 490 K. STM images showed that a second structure with \(p(4 \times 5\sqrt{3})\) spacing was formed.

In 2006, a new model for the \(p(4 \times 4)\) was proposed by the groups of Besenbacher and Varga.\textsuperscript{82,83} The model, shown in Figure 4 (A), is composed of pairs of back to back triangle hexamers of Ag atoms. Two O atoms are located in a furrow between each pair of Ag hexamer triangles. Varga’s group used a combination of STM, surface x-ray
diffraction, core level spectroscopy, and DFT to develop their model. Besenbacher’s group used a combination of STM and DFT. In addition to the $p(4 \times 4)$ structure, they also identified a $c(3 \times 5\sqrt{3})$ structure. They proposed a model for this structure (Figure 4 (B)) that was also composed of Ag hexamer triangles, but with a different arrangement. In a later paper, Besenbacher’s group also identified a $c(4 \times 8)$ structure and proposed a model for that and for the $p(4 \times 5\sqrt{3})$ structure first seen by Carlisle. Shown in Figure 4(C), the model has Ag hexamer triangles, and also two Ag decamer triangles.

Subsequent studies by other groups have confirmed many aspects of these models. Klust and Madix used CO to remove O from a $p(4\times4)$-O/Ag(111) surface at room temperature. After O was removed, the Ag atoms coalesced into islands. From the size of the islands, they calculated that each $(4 \times 4)$ cell contained 12 Ag atoms, in agreement with the Besenbacher and Varga models. Also, a LEED and LEEM study of a

![Figure 4. Models of O/Ag(111) structures. (A) $p(4 \times 4)$; (B) $c(3 \times 5\sqrt{3})$; (C) $p(4 \times 5\sqrt{3})$; (D) $c(4 \times 8)$. Light grey balls are substrate Ag atoms. Darker grey balls are Ag atoms in overlayer. Red balls are O atoms. Darkest atoms in (D) are Ag atoms visible in STM images.](image-url)
A (4×4) surface formed by dosing Ag(111) with NO₂ at 500 K supported a model of two Ag hexamer triangles. Finally, a 2014 paper by Lundgren’s group using STM, XPS, and DFT provided support for the model of the c(4 × 8) structure seen by Besenbacher and colleagues.

The nature of the oxygen species adsorbed to silver surfaces is a key component in many heterogeneously catalyzed reactions such as the epoxidation of ethylene and the partial oxidation of methanol. Although multiple O/Ag(111) surface structures have been identified, many questions about the nature of O surface and subsurface species remain. In the work presented here, NO₂ and atomic oxygen were used to study the impact of sample temperature and oxygen source on the formation of O/Ag(111) surface structures and the formation of subsurface oxygen. With AO dosing, the nature of the surface showed significant differences depending on the flux and energy of incident gas-phase oxygen atoms. When a lower temperature filament was used to generate AO, the surface oxides previously reported were observed. When O was deposited with a higher filament temperature, the surface became highly corrugated, little subsurface oxygen was observed, and thin layers of Ag₂O appeared to form. These results show that the energy and flux of oxygen are important parameters in the chemical identity and abundance of oxygen on silver surfaces and suggest that formation of the Ag₂O thin film hinders formation of subsurface oxygen.

The effect of sample temperature on oxygen induced surface reconstruction and subsurface oxygen incorporation was also studied. The Ag(111) surface was dosed with NO₂ and AO at temperatures ranging from 475 K to 525 K. For short AO doses, sample temperature had minimal effect on surface reconstruction. For longer doses, changes in
sample temperature in the range of 490 K to 525 K had a substantial impact on surface reconstruction and subsurface oxygen absorption. At higher temperatures, $c(3 \times 5\sqrt{3})$ and $p(4 \times 5\sqrt{3})$ structures were most prevalent and TPD data showed that little or no $O_{\text{sub}}$ formed. At lower temperatures, $c(4 \times 8)$ structures were common for intermediate dose lengths. As the dose length increased, extended chains formed across the surface. For long doses at temperatures $\leq 500$ K, the entire surface was covered in a new structure. TPD data showed that significantly more than 1.0 ML of oxygen was present, indicating that substantial $O_{\text{sub}}$ was formed.
CHAPTER TWO

EXPERIMENTAL METHODS

All experiments were performed in an ultrahigh-vacuum scanning tunneling microscope (UHV-STM) system that consisted of three isolatable chambers; the system is depicted in Figure 5. The three chambers are (a) a small load lock chamber; (b) the UHV STM chamber; and (c) a UHV preparation chamber. Each of the chambers and their relevant equipment are briefly described. The load lock allowed for the transfer of samples and STM tips from ambient conditions to the UHV chambers without breaking vacuum in the remainder of the system. It was separated from the STM chamber with a 2 3/4” manual gate valve (VAT), and could be baked separately from the rest of the system. It was equipped with a 12” magnetically coupled transfer arm (Thermionics). The load lock was pumped by an 80 Ls$^{-1}$ turbomolecular pump (TMP) (Leybold Turbovac SL80) backed by a mechanical forepump. The base pressure was typically in the 10$^{-9}$ Torr range after pumping down from atmospheric pressure overnight.

The central UHV chamber housed a low-temperature STM (Pan Scan, RHK Technology), and its base pressure was 4.0 × 10$^{-11}$ Torr. The UHV chamber was pumped by a 300 Ls$^{-1}$ ion pump (Gamma Vacuum, TiTan 300T) and was equipped with a quadrupole mass spectrometer (QMS) for residual gas analysis (ExTorr XT200M). During initial experiments, the STM was connected to a flow cryostat and cooled with liquid nitrogen (LN$_2$). With the flow cryostat, the STM could be cooled to 80 K and
remained stable for several days. For later experiments, the flow cryostat was replaced with a closed cycle He cryostat. With the closed cycle cryostat, the STM was cooled to 20 K and remained stable indefinitely. A wobble stick (Ferrovac) was used for insertion of samples or tips into the microscope. It was also used to transfer samples between the STM, storage rack, the load-lock transfer arm, and the prep chamber manipulator. The STM was controlled with a PC connected to a RHK R9 controller. Temperatures were measured using Si diodes mounted on the STM connected to a Prevac Heat 2PS. The STM chamber was also equipped with five tip storage slots and a Ta filament for heat treating of the STM tips. There were also seven sample storage slots; one had contacts for resistive heating, and another had contacts for radiative heating with a special insert.

Figure 5. UHV-STM system. (L) Schematic of the UHV-STM experimental apparatus consisting of three isolatable chambers. (R) Image of chambers, pumps, and supporting electronics.

The preparation/analysis chamber is the third chamber in the system. This is a UHV chamber with a base pressure around $2.0 \times 10^{-10}$ Torr and is pumped by a 300 Ls$^{-1}$ magnetically levitated TMP (Edwards STP 301) and a 150 Ls$^{-1}$ ion pump (Gamma Vacuum, TiTan 150T). The chamber is equipped with a QMS (UTI 100C) for residual gas analysis and TPD. The control and signal processing for the QMS were done with
The chamber also has a cylindrical mirror analyzer (Physical Electronics, 10-155) for AES surface analysis and a sputter gun (RBD Instruments, IG-2) for sample preparation. The chamber also has three leak valves and a directed doser for controlled introduction of gases such NO$_2$ into the UHV chamber. The sample was positioned, as well as heated or chilled, on a four-axis manipulator (McAllister Technical Services, MB-1520) that could also bring the sample into the STM chamber. The manipulator has a differentially pumped rotary stage that was pumped by a small ion pump (Gamma Vacuum, TiTan 20s). With LN$_2$ flowing through the cooling loop, the base temperature for the sample was 90 K. The temperature was controlled with a Eurotherm 2404 PID controller that regulated the current flow through a thoriated W filament behind the sample (Kepco ATE 6-10M power supply). The sample could be biased up to 1 kV with respect to the heating filament by a Kepco BHK 2000-0.1M power supply for electron bombardment heating up to at least 1,600 K.

Figure 6. Manipulator and sample holder. (L) Ag(111) sample mounted on Ta holder and inserted into the manipulator arm. (R) Ag(111) sample and Ta holder on benchtop. The wires visible on the right are the leads of the K type thermocouple.
One Rh(111) crystal and two Ag(111) crystals, from Surface Preparation Laboratory, were used in the experiments. The crystals were 10 mm × 6 mm rectangles and 1.5 mm thick. They were cut to a “top-hat” shape leaving 1 mm wide brims at each end. The crystals were mounted on Omicron-style Ta sample holders and suspended by two 0.5 mm diameter Ta wires (Advent Materials) over a 12 mm × 8 mm rectangular window cut through the holder. The holders also had four electrical contacts that aligned with contacts in both the sample receiver in the manipulator and inside the STM. Two of the contacts were isolated and used for the leads of the type-K thermocouple welded to the crystals. The remaining two contacts were shorted to the sample holder.

Having three isolatable chambers allowed samples and STM tips to be introduced into the system, cleaned, prepared, and analyzed without breaking UHV conditions in the STM chamber. After being brought in through the load lock, samples were transferred through the STM chamber and into the preparation/analysis chamber. In the preparation/analysis chamber, samples could be held at any temperature from 90 K to 1,600 K. Samples were cleaned in the preparation/analysis chamber through repeated cycles of Ar+ sputtering and annealing. AES and LEED instruments in the chamber were used to confirm that the samples were properly cleaned. After cleaning, the samples were dosed using O\textsubscript{2}, NO\textsubscript{2}, or AO. After dosing, samples could be analyzed by AES, LEED, or TPD in the preparation/analysis chamber. By performing all sample cleaning and preparation in the preparation chamber, the residual gases and other impurities were isolated from the STM chamber. This kept the STM chamber clean and allowed long periods of imaging with minimal accumulation of impurities on the surface.
Although the two chambers were isolated by a gate valve, the same holder was used for the preparation/analysis chamber manipulator and STM. This meant that samples could be moved between the STM and the preparation/analysis chamber while maintaining UHV conditions. After dosing, AES and LEED could be used to analyze a sample before STM imaging. Also, AES, LEED, and TPD experiments could be done on samples after STM imaging. This allowed STM imaging, which showed small-scale detailed structures, to be directly connected with the results of wider scaled ensemble averaging techniques such as AES, LEED, and TPD.

**STM Theory**

Scanning tunneling microscopy is based on the quantum mechanical tunneling of electrons. Tunneling refers to a particle crossing a barrier that it could not surmount classically and can be traced to earliest days of quantum mechanics. The design of the first STM derived from Young’s work at NIST on a scanning field emission microscope called a topografiner which had a lateral resolution of about 400 nm. Working at IBM Zurich, Gerd Binnig and Heinrich Rohrer developed the first STM in 1981. One of the original goals for the instrument was to achieve resolution of the structure of silicon, which was being debated at the time, but the first atomic scale images were of CaIrSn$_4$ and Au. Soon after, Binnig and Rohrer were able to obtain atomically resolved images of the (7 × 7) reconstruction of Si(111) and in 1986 Binnig and Rohrer were awarded the Nobel Prize in Physics.
In an STM, electrons tunnel across a vacuum barrier between a sharp metal tip and a conducting or semiconducting sample. A one dimensional model of quantum mechanical tunneling in an STM is shown in Figure 7. Classically, an electron traveling between the tip and the sample would require an energy larger than the work function of the tip or sample to cross the barrier. However, due to the wavelike nature of particles, there is a finite probability that an electron can cross the barrier. A precise mathematical model of tunneling current needs to consider the work functions of the tip and sample and the tip geometry. However, a simpler equation can show tunneling current as a proportion. For one dimension, the wave function of an electron at a junction with a rectangular barrier is:

$$\psi(z) = \psi(0)e^{-kz}$$

where: $\psi$ is the electronic wave function and $z$ is the distance between the tip and sample.
\[ \kappa = \sqrt{\frac{2m(V-E)}{\hbar}} \]

where: \( m \) is the mass of an electron; \( V \) is the potential in the barrier, and \( E \) is the energy of the electron. The transmission probability is proportional to the tunneling current \( I(z) \), and is given by:

\[ I(z) \propto e^{-2\kappa z} \]

Although an electron has a finite probability of penetrating a barrier, the probability is exponentially dependent on distance. For a small bias, \((V-E)\) can be approximated as the work function \((\Phi)\) of the metal, which is typically around 5 eV.\(^{95}\) For every 1 Å change in distance between the tip and sample, the tunneling current decreases by approximately an order of magnitude. This exponential decay of current over atomic scale distances enables atomic resolution with STM.\(^{96}\)

If the tip and sample have the same work function \( \Phi \), electrons have an equal probability of tunneling in either direction and there would be no net current. Applying a bias voltage \((V)\) offsets the Fermi levels. The polarity of \( V \) determines the net direction electrons flow. By convention, the tip is regarded as grounded. If \( V \) is positive, there is a net flow of electrons from the tip to the sample. If \( V \) is negative, there is a net flow of electrons from the sample to the tip.\(^{97}\) To record an image, the STM tip is rastered across a surface by piezoelectric ceramics. Two different imaging modes can be used. In constant-height mode, the vertical position of the tip is held constant while the surface is scanned and the current is recorded. In constant current mode, a feedback loop attempts
to maintain a pre-set current by adjusting the vertical position of the tip during scanning. The image depends on both the structure and the local density of states (LDOS) of the tip and sample.\textsuperscript{94} All of the images in this dissertation were recorded in constant current mode.

Tip preparation

Reliable fabrication of atomically sharp tips has been an issue since the development of the STM. Approaches to tip fabrication range from simple cutting to ion-milling\textsuperscript{98} and electrochemical etching.\textsuperscript{99,100} For this research, a new method of fabricating atomically sharp Pt/Ir and W tips was developed.\textsuperscript{101} The objective was to use an electrochemical technique to fashion high quality tips with common, inexpensive equipment. Electrochemical etching was attractive because it had been demonstrated to be effective in fashioning tips from many materials and for many applications.\textsuperscript{102,103} Although the method developed was effective for both Pt/Ir and W tips, only Pt/Ir tips were used for the STM images presented here.

Electrochemical etching yields highly tapered tips with an extremely small radius of curvature because the etching rate of a wire dipped into an electrolytic solution is not uniform across the wire.\textsuperscript{104,105} When the tip wire is inserted into the solution, a meniscus forms, jutting up from the liquid surface. When an electric potential is applied to the tip wire, there is a concentration gradient of etchant ions within the meniscus that results in a vortex of the etchant ions about the tip apex as etching proceeds. The concentration of etchant ions is lowest at the top of the meniscus and increases progressively toward the
base. During the etching process, the etching rate is faster at the base of the wire than along the sides.

The pulsed alternating current etching technique developed for this research used a variable AC power source (Variac) to set the alternating current (AC) potential, a graphite counter electrode (1 cm diameter graphite rod, McMaster-Carr), a custom made glass etching vessel (Allen Scientific Glass), and an Arduino Uno microcontroller to control the number and duration of AC pulses. The apparatus is depicted in Figure 8. The glass-etching vessel held \( \approx 100 \) mL of etching solution. The vessel design was similar to the apparatus presented by Hagedorn et al.\(^{106}\) A 15 mm diameter glass cylinder, with both the top and bottom open, was fused to the inner wall of the vessel. The cylinder was 15 mm deep, and the vessel was filled so the liquid level was below the top of the small cylinder which dampened any surface disturbances during etching.

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Figure 8. Electrochemical etching station. (A) Illustration of the electrochemical etching station showing the electrodes and arrangement of etching solution reservoirs; (B) Photograph of the glass etching container; (C) diagram of etching control circuit.
The Arduino Uno microcontroller was connected to a simple transistor and relay circuit, shown in Figure 8 C). One of the digital I/O pins on the Arduino Uno was used to activate a 2N2222 transistor. The transistor, in turn, controlled a relay (Quaz-SS-105D) that switched the current flow from the Variac. The Arduino Uno microcontroller and circuit delivered AC voltage pulses of 0.5 s duration every 2 seconds. The desired number of AC pulses was set in the software for tip fabrication once the optimal number of AC pulses was obtained. Pulse duration and frequency, as well as the potential and frequency of the AC in the pulse were measured during the etching process with a digital oscilloscope with 1 MΩ input impedance, and the RMS AC potential was verified with a handheld multimeter. No undesired switching of the relay due to the etching current load or any extraneous pulses from noise in the circuit was observed, and the pulse duration was largely invariant for all of the trials.

Pt/Ir tips were fabricated from 0.25 mm diameter Pt/Ir wire (80% Pt, 20% Ir) (Advent Materials) using 1.0 M CaCl₂ (Aldrich, 99%) as the etching solution. Etching of high-quality Pt/Ir tips required two etching stages; an initial coarse stage using continuous AC power followed by a fine stage using pulsed AC etching. Using only pulse etching was possible, but the process was too slow to be of practical use. Continuous AC etching without the pulsed etching stage resulted in tips with a bulbous deposit at the apex. An SEM image of a Pt/Ir tip fabricated using only continuous AC is shown in Figure 9.
Combining a coarse etching stage using continuous AC with a fine etching stage using pulsed AC produced atomically sharp tips reliably and efficiently. The coarse etching provided the gross shape, but left the bulbous mass. After coarse etching, the pulsed AC etching stage was used to remove the bulb. A benefit of using the two stage approach was that it allowed a higher potential to be used during the coarse etching stage, reducing the overall etching time.

The coarse etching stage was based on a method developed at Argonne National Labs and consisted of three different voltage steps (NST-SOP-122, Rev. 3). The tip was first etched for 100 s using a continuous AC potential of 35 V (RMS). The potential was then dropped to 30 V RMS for 50 s, and finally 28 V until the tip was almost entirely etched away and bubbling ceased. After coarse etching, the tip was inserted 2-3 mm deeper into the solution for fine etching. The optimal fine pulse etching parameters were determined by varying the number and voltage of the pulses. Figure 10 shows SEM images of Pt/Ir tips fabricated with different pulsed etching parameters. The optimal
parameters for the pulsed etching stage were found to be 5 pulses of 0.5 s at 2.5 V AC. These conditions yielded >80% sharp, symmetric tips.

Figure 10. SEM images of Pt/Ir tips after coarse and fine etching. If either the number of pulses or the voltage was too low, the bulbous formation at the apex was not removed. If the number of pulses or the voltage was too high, the apex was blunted. White scale bars are 10 μm in all images.

**Low energy electron diffraction**

Low energy electron diffraction uses the wave like properties of electrons to determine the surface structure of crystalline materials and adsorbate layers. In 1924, de Broglie proposed that particles have a wavelength based on their momentum:

$$\lambda = \frac{h}{p}$$
where $\lambda$ is the wavelength, $h$ is Planck’s constant, and $p$ is the particle’s momentum. A few years later, Davisson and Germer confirmed de Broglie’s hypothesis when they observed the diffraction of electrons by a Ni(111) crystal. Using de Broglie’s equation, electrons with energies in the range of 20-200 eV have wavelengths from 2.7 Å to 0.87 Å, which is on the order of atomic spacing.

Figure 11. Schematic drawing of LEED instrument. The electron gun is aligned normal to the crystal surface. The fluorescent screen is semi-transparent, allowing the diffraction spots to be observed through the window.

The LEED instrument, shown schematically in Figure 11, has an electron gun for producing a parallel, monoenergetic beam of electrons. The electron beam is directed at a normal angle to the surface. Electrons scattering elastically from the surface impact a hemispherical fluorescent screen. A series of grids is located between the sample and the screen to remove inelastically scattered electrons. The first grid is grounded to provide a
field free area to reduce electrostatic deflection. The second and third grids have a negative potential slightly below the energy of the electrons. The fourth grid is also usually grounded. The combination of grids allows elastically scattered electrons to pass while blocking inelastically scattered electrons. Elastically scattered electrons which pass the grids are then accelerated onto the fluorescent screen by a large positive voltage. The impact of the electrons causes the fluorescent screen to glow, and the diffraction pattern is recorded by a camera outside of the UHV chamber.

Diffraction spots form due to interference between electrons. Constructive interference occurs when the Bragg equation is satisfied. This happens when the difference in path length between two waves is an integral number of the wavelength.

\[ n\lambda = d \sin(\theta) \]

The equation shows that \( \sin(\theta) \) is proportional to \( 1/d \). This means that a larger distance between objects will create smaller diffraction pattern. \( \sin(\theta) \) is also inversely related to the energy of the incident electrons.

Figure 12. Constructive interference for two waves. Two waves will only constructively interfere when the path lengths are equal.
The observed LEED pattern is a scaled version of the reciprocal lattice. The reciprocal lattice is based on the surface structure unit cell. If the surface structure unit cell is defined by vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, the vectors of the reciprocal lattice can be found by:

$$\mathbf{a}_1^* = 2\pi \frac{\mathbf{a}_2 \times \mathbf{n}}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{n})} \quad \quad \mathbf{a}_2^* = 2\pi \frac{\mathbf{a}_1 \times \mathbf{n}}{\mathbf{a}_2 \cdot (\mathbf{a}_1 \times \mathbf{n})}$$

where $\mathbf{n}$ is a vector normal to the surface. As an example, Figure 13 shows a model of an fcc(110) surface and the reciprocal lattice.

![Real and reciprocal lattice of an fcc(110) surface. The symmetry of the real space lattice is retained, but the spacing changes.](image)

Figure 13. Real and reciprocal lattice of an fcc(110) surface. The symmetry of the real space lattice is retained, but the spacing changes.

An advantage of LEED for surface science is that it is inherently surface sensitive. For example, at 55 eV, the inelastic mean free path for an electron in Rh is 4.57 Å (NIST: SRD 71). That is slightly less than two atomic layers in a Rh crystal, so the probability for an electron to penetrate more than a few layers into the bulk and back out is very small. As a result, the vast majority of the electrons detected with LEED are diffracting from the surface or the very near subsurface.

Although LEED can be used quantitatively in some cases, for the experiments in this dissertation, LEED was only used qualitatively. The spot size the electron beam
hitting the surface of the crystal was approximately 0.5 mm in diameter. As a result, the LEED patterns observed were the result of the superposition of structures present in an area more than a million atoms wide. In contrast, the STM images presented here show areas in the range of 10 atoms to several hundred atoms across. One benefit of this is that LEED can provide qualitative information about the uniformity of the surface. LEED images showing only a single diffraction pattern provide strong evidence that large areas of the surface have the same structure. LEED images showing complex diffraction patterns could be evidence of multiple structures or a single complex structure. STM imaging can then be used to distinguish those possibilities.

**Auger electron spectroscopy**

Auger electron spectroscopy is a technique for the chemical analysis of surfaces. The Auger electron process was discovered independently by Lise Meitner and Pierre Auger. The process is depicted in Figure 14. The first step of the Auger process occurs when a core hole is formed by the ionization of a sample atom. Either X-rays or high energy electrons can be used to remove the core electron. The instrument used for this dissertation used an electron gun. Removal of the core electron is most efficient when the energy of the impinging electrons is several times higher than the binding energy of the core electron. In the next step, the core hole is filled by a higher energy electron from an outer shell. The transition releases energy corresponding to the difference between the two levels in one of two possible ways: an X-ray photon or by transfer to another electron. If the energy is transferred to another electron, that electron, referred to as an Auger electron, is emitted.
Figure 14. Auger electron process. A high energy electron removes a core electron, leaving a hole. The hole is filled by an electron from a higher energy orbital, transferring energy to another electron, which is emitted.

The energy of the emitted electron depends only on the energy levels of the sample atom, and not on the energy of the electron that initiated the process. Although both X-ray fluorescence and Auger electron emission are possible, only one process can occur after the initial ionization. The probability of Auger electron emission depends strongly on the atomic number of the target atom. For atoms with a lower atomic number, Auger emission is more probable than X-ray fluorescence. However, because the Auger process requires 3 electrons, very light elements will not be detected.\textsuperscript{112}

Figure 15. Schematic diagram of AES instrument. The energy of electrons able to reach the detector is determined by an electric field which is generated between the inner and outer mirrors. Electrons ejected from the sample pass through an opening and into the region between the mirrors. Electrons with lower energy are pulled into the inner mirror before reaching the opening to the detector. Electrons with higher energy pass travel past the opening.
A diagram of an Auger spectrometer is shown in Figure 15. The instrument used for this research had a cylindrical mirror analyzer (CMA). Inside the CMA, there are two concentric cylinders, with openings at the front and rear of the inner cylinder. The inner cylinder is grounded while the outer cylinder has a variable negative potential. For a given magnitude of negative potential, only electrons with a particular energy will travel on a trajectory which will allow them to pass through the rear slit. The analyzer sweeps across a specified range of electron energies, and the electrons reaching the detector are counted. Due to high background noise, AES spectra are typically reported as a derivative.

**Temperature Programmed Desorption**

In temperature programmed desorption, sometimes called Thermal desorption spectroscopy (TDS), the temperature of a sample is increased linearly under UHV conditions while the partial pressures of desorbing species are recorded. As the temperature of the sample increases, energy increases so the probability that an adsorbate will desorb increases. If the activation barrier for desorption is independent of coverage, the rate constant shows Arrenhius behavior:

\[
k_d = A e^{\left(\frac{-E_d}{RT}\right)}
\]

where \(A\) is a pre-exponential factor and \(E_d\) is the desorption energy.\(^{113}\) A rate equation for desorption is known as the Polanyi-Wigner equation:
\[ r(\theta) = -\frac{d\theta}{dt} = \nu(\theta)\theta^n e^{-\frac{E_d(\theta)}{RT}} \]

where \( r(\theta) \) is the rate of desorption, \( \theta \) is the surface coverage, \( t \) is time, \( \nu \) is a pre-exponential factor, and \( n \) is the order of desorption.\(^{114}\) The Polanyi-Wigner equation relates the rate of desorption of a gas to the temperature, the surface coverage, and the order of desorption.\(^ {115}\) Zero order kinetics means that the rate of desorption does not depend on coverage and also that the rate of desorption increases exponentially with temperature. Because there is a finite quantity of adsorbate, a zero order peak will drop sharply after increasing exponentially to the temperature of maximum desorption (T\(_{\text{max}}\)). Zero order TPD spectra with different \( \theta \) have a common leading edge, but T\(_{\text{max}}\) will increase as \( \theta \) increases. Zero order desorption is associated with multi-layer adsorbates or situations where there is an excess of reactants which can continuously replenish limited desorption sites.\(^{116}\)

Figure 16. Simulated desorption peaks. Zero order desorption peaks have a common leading edge. First order is asymmetric, with a common T\(_{\text{max}}\). For second order, the T\(_{\text{max}}\) decreases with increasing coverage.
In first order desorption, the rate of desorption depends linearly on $\theta$. $T_{\text{max}}$ is independent of coverage, but does depend on heating rate. First order desorption is associated with direct desorption from sub monolayer coverage. With second order desorption, the rate of desorption depends on the square of $\theta$ and $T_{\text{max}}$ decreases with increasing $\theta$. Second order desorption is associated with recombinative desorption.

**Atomic oxygen source**

For atomic O dosing, O atoms were produced by thermally cracking O$_2$ molecules over a hot Ir filament.$^{117}$ Ir was chosen for the filament to avoid potential problems related to oxidation of W filament.$^{118}$ Ir wire (Advent Materials) was formed into a double loop and attached to two copper barrel connectors. Current to the filament was controlled by an alternating current Variac. The temperature of the Ir filament was determined using a ‘disappearing filament’ pyrometer.$^{119}$ At the lower setting, the filament temperature was approximately 1,750 K. At the higher setting, the filament temperature was approximately 2,000 K. Prior to dosing, the Ir filament was heated at $>2,000$ K for several minutes to remove contaminants. When dosing with AO, the crystal was brought within 0.5 cm of the filament. Using a combination of LN$_2$ and radiative heating, the temperature of the crystal could be held constant throughout dosing. To dose with AO, the chamber was backfilled with O$_2$ using a leak valve. Throughout dosing, a flow of O$_2$ was fed into the chamber and the TMP was also running. This ensured that there was a continuous flow of O$_2$ in the chamber.

Multiple tests were conducted with AES, TPD, and STM to confirm that only O species were generated by the filament. After all experiments, no Ir was ever observed in
the Auger spectra. To further test if Ir was deposited, the filament was set to 2,000 K, and the chamber was backfilled to $1 \times 10^{-6}$ Torr of Ar. A clean Ag(111) surface was exposed to the hot filament for 10 min. No Ir was seen with AES. The chamber was then backfilled to $1 \times 10^{-6}$ Torr O$_2$ for 10 min, without the Ir filament, and TPD was taken of the surface. No O$_2$ desorption was observed up to 950 K. O$_2$ readily dissociates on Ir, and if appreciable Ir were deposited, O$_2$ desorption should be observed. Other studies using Ir filaments to generate AO have also reported no appreciable Ir accumulation from a hot Ir filament.

![Figure 17. Ir filament and AES spectra of clean and dosed Ag(111). (L) Image of the Ir filament being heated. (R) AES spectra before and after AO dosing on Ag(111). The only visible difference is the formation of an O peak near 500 eV. No Ir or C contamination was detected after dosing.](image)
CHAPTER THREE

OXYGEN ADSORPTION AND ABSORPTION ON RH(111)

The reactivity and selectivity of Rh surfaces depend on the electronic and geometric surface structures that result from a balance of attractive and repulsive forces among adsorbate and substrate atoms. In the case of O adsorption, the balance of forces yields periodic, well-defined arrangements with little reconstruction. Due to its high price and scarcity, Rh is typically divided into nanoparticles to increase specific surface area when it is used as a catalyst. Many Rh catalyzed reactions have also been shown to be sensitive to the crystallographic plane of the catalyst, which depends on the size and shape of the catalyst. Because Rh is an fcc metal, the 111 face is most stable, and is therefore believed to be the predominate plane on nanoparticles. For this project, a Rh(111) crystal was used to study the adsorption and absorption of AO on rhodium.

Oxygen adsorbing on Rh(111) has been widely studied. Based on LEED, O₂ adsorbing on Rh(111) was originally thought to yield a (2 × 2) structure. However, subsequent publications suggested that the (2 × 2) structure would be virtually indistinguishable from three (2 × 1) domains rotated by 60°. The current model is that at low coverages O atoms are initially dispersed across the surface, but islands of (2 × 2) nucleate with increasing Oₐd. When θₒ approaches 0.25 ML, the (2 × 2) structure predominates, but the surface does not saturate. With further O dosing, the surface becomes less ordered as (2 × 2) domains are converted into (2 × 1) domains by the
insertion of $O_{ad}$. The surface saturates at 0.5 ML, and consists of $(2 \times 1)$ domains oriented along 1 of 3 axes rotated by $60^\circ$.

![Models of (2 x 2) and (2 x 1) O/Rh(111) structures. (A) (2 x 2) structure. $\theta_O$ is 0.5 ML at saturation. (B) (2 x 1) structure. $\theta_O$ is 0.25 ML at saturation. Gray balls are Rh and red balls are O atoms on fcc surface sites.](image)

In order to validate the UHV-STM system and to confirm the presently accepted model of $O_2$ adsorption on Rh(111), experiments were done with $O_2$ before proceeding to AO dosing. AES data was used for O surface coverage, while TPD data quantified the total amount of both $O_{ad}$ and $O_{sub}$. The Rh(111) crystal (Surface Preparation Laboratory) was 1.5 mm thick and 10 mm x 6 mm. The Rh crystal was initially cleaned by repeated cycles of Ar+ sputtering at room temperature followed by annealing for 10 min at 1,150 K. Approximately every five cycles the crystal was further cleaned by exposure to $O_2$ at $1 \times 10^{-8}$ Torr and 900 K for 5 min. Cycles were repeated until surface impurities were below the detection of the AES. Surface cleanliness was also confirmed by LEED, TPD and STM imaging. Figure 19 shows a LEED image and AES spectra taken after cleaning.
Figure 19. LEED and AES of clean Rh(111). The LEED image, taken at 62 eV, shows sharp spots indicative of a clean surface.

Between experiments, the crystal was again cleaned by Ar+ sputtering for 5 min followed by annealing for 5 min at 1,150 K per standard cleaning procedures.\(^{129}\) To dose with O\(_2\), the chamber was backfilled with \(1.1 \times 10^{-6}\) Torr of O\(_2\). During dosing, the sample temperature was held constant at 320 K by a combination of radiative heating and LN\(_2\) cooling. For TPD experiments, the dosed sample was heated at a rate of 4 K s\(^{-1}\) by radiative and e\(^-\) beam heating on the back face of the sample. The temperature of the sample was monitored by a K-type thermocouple spot-welded to the edge of the crystal.

Figure 20. Graph of AES O:Rh ratios. The ratio of O:Rh initially increases rapidly. By 20 L, the ratio of O:Rh plateaus, showing that the surface has become saturated.
The Rh(111) crystal was exposed to O₂ doses from 0.5 L to 500 L at 320 K. Figure 20 shows a graph of the ratio of the O peak at 503 eV to the Rh peak at 303 eV for a series of doses. Initially, the ratio increases rapidly as the dose amount is increased. This shows that at 320 K, O₂ has a very high sticking probability for dissociative adsorption on bare Rh(111). However, the rate of increase in the ratio of O to Rh begins to slow by 10 L. By 20 L, the ratio of O to Rh reaches a plateau. Between 20 and 45 L there only a slight increase at 45 L, suggesting the surface has become saturated.

Figure 21. TPD spectra after O₂ dosing on Rh(111). The 30 (blue) and 500 (black) L curves are virtually the same. This shows that the surface is saturated after 30 L. Sample temperature was 320 K, ramp rate = 4 Ks⁻¹.

Saturation of the surface with O₂ dosing was further supported by TPD measurements. Figure 21 shows TPD spectra taken after exposing the Rh(111) crystal to O₂. The data agree with previous experimental and theoretical studies showing O₂ desorbs from Rh(111) in a broad peak spanning 800 to >1,300 K. Exposure of 1.5 L of O₂ yielded a small, broad desorption peak (red trace) corresponding to θ₀ = 0.25 ML.
With higher doses, the leading edge of the desorption peak shifted from about 1,000 to 800 K, but the intensity of the peak was unchanged. The desorption spectra from O₂ exposures of 30 L (blue trace) and 500 L (black trace) were very similar, indicating that extended dosing with O₂ at 320 K does not result in the accumulation of more oxygen.

Figure 22. STM image of (2 × 1) structures on Rh(111). Image taken after 40 L dose of O₂ at 320 K showing three (2 × 1) domains. On the right side is a domain running parallel to the horizontal scan direction. On the left, is another domain rotated 60°. A third domain, in the upper right, is rotated 120° from horizontal. Tₛ = 80 K, Iₜ = 0.93 nA, V₃ = 250 mV.

STM was then used to study the nature of the surface after saturation dosing. In order to insure the surface was saturated, the Rh(111) crystal was exposed to 40 L of O₂ at 320 K to achieve θₒ = 0.5 ML. Figure 22 shows an STM image after dosing the surface with 40 L of O₂ at 320 K. This image shows that at θₒ = 0.5 ML, (2 × 1) adlayers were the predominant oxygen structures, agreeing with the observations made by
Marchini et al.\textsuperscript{47} Three $(2 \times 1)$ domains, each rotated by $60^\circ$, are visible in the image. The area on the right of the image shows the stripes of a $(2 \times 1)$ structure at $0^\circ$ in relation to the horizontal fast scan direction of the tip. The left side of the image shows $(2 \times 1)$ structure at $60^\circ$ relative to the horizontal fast scan direction. On the right, near the top of the image is a smaller domain $120^\circ$ relative to the horizontal fast scan direction of the tip. After calibrating the STM piezos and correcting for scaling inaccuracies, the periodicity of the rows along the edge of the unit cell was $5.77 \pm 0.28$ Å, in reasonable agreement with the expected value of $5.43$ Å, twice the interatomic distance of atoms in Rh(111).\textsuperscript{132} The distance between atoms along the rows was $2.84 \pm 0.15$ Å, close to the expected distance of $2.72$ Å.\textsuperscript{133}

The STM images are in agreement with Marchini et al., among others, that O preferentially forms $(2 \times 1)$ structures rather than $(2 \times 2)$ structures at saturation dosing. Based on STM images, over 90\% of the surface was covered with $(2 \times 2)$ domains after dosing with O$_2$. However, as seen in Figure 23, STM images also showed that smaller $(2 \times 2)$ domains were present, intermixed among larger $(2 \times 1)$ domains. An example of a $(2 \times 2)$ domain can be seen in the lower left of Figure 23. For all O$_2$ exposures yielding $\theta_0 = 0.5$ ML, similar hexagonal patches were observed. The lengths of the sides of a parallelogram aligned with interatom spacing in these $(2 \times 2)$ areas was found to be $5.80 \pm 0.15$ Å $\times 5.80 \pm 0.15$ Å, consistent with a $(2 \times 2)$-O adlayer. A close-up of the $(2 \times 2)$ domain is shown in Figure 24. A lattice is overlaid on part of the image, showing the hexagonal symmetry.
Figure 23. STM image of (2 × 1) and (2 × 2) structures on Rh(111). (2 × 1) domains are visible on the top and right of the image. A (2 × 2) domain is in the lower left. $T_s = 80$ K, $I_T = 0.93$ nA, $V_b = 250$ mV.

Figure 24. STM image of (2 × 2) domain on Rh(111). The white overlay shows the hexagonal symmetry of the (2 × 2) structure. $T_s = 80$ K, $I_T = 0.93$ nA, $V_b = 250$ mV.
A typical LEED image of the saturated surface is shown in Figure 25. The Rh(111) crystal was dosed with 40 L of O$_2$ at 320 K, the same dose as the images in Figures 22-24. The reciprocal unit cell vectors for the (2 × 1) structure are indicated by the arrows. As discussed above, the LEED pattern could be consistent with either three (2 × 1) structures or a single (2 × 2) structures. However, the sharpness of the pattern is evidence that the surface is well-ordered over large areas. STM images can show atomic scale detail, but only for small areas. The LEED images suggest that atomic order visible in the STM images is representative of the entire surface.

Figure 25. LEED image of Rh(111) surface after O$_2$ dosing. The arrows indicate the reciprocal unit cell vectors for the (2 × 1) structure. Image taken after dosing with 40 L O$_2$ at 320 K. Energy = 62 eV.

Previous authors have suggested that a (2 × 2) structure on Rh(111) could be the result of CO contamination, rather than a (2 × 2)-O pattern.$^{47}$ This possibility was investigated using AES and TPD. The UHV-STM system used for these experiments allowed the sample to be transferred between the STM chamber and the preparatory
chamber. This allowed AES and TPD experiments to be done on the sample after STM imaging. A typical AES spectra taken after a dose where hexagonal patches was observed is shown in Figure 26. No evidence of a carbon peak near 280 eV was seen under any of the O$_2$ dosing conditions employed. The two Rh peaks close to 280 eV are essentially the same before and after dosing, other than a small decrease due to O adsorption. Also, during TPD measurements, m/z = 44 (CO$_2$+) and 28 (CO+) were recorded; no desorption peaks were observed for either species. Finally, a lower-temperature TPD ramp (starting at 300 K) was used, and again, no desorption indicating CO or CO$_2$ was observed. The absence of CO or CO$_2$ desorption indicates that there was no appreciable CO adsorption to the surface, and that the hexagonal structures observed were (2 × 2)-O.

Figure 26. AES spectra before and after O$_2$ dosing. There is a slight decrease in the Rh peak which is consistent with an adlayer forming. The lack of change in the curve near 280 eV shows that no C was adsorbed to the surface.

The STM results here differ somewhat from the model proposed by Marchini et al. because both (2 × 2) and (2 × 1) structures were observed. However, (2 × 2)
structures were significantly less prevalent, making up less than 10% of the surface area at saturation. Rather than contradicting Marchini et al., the STM and TPD results here support the finding that the $(2 \times 1)$ structure is significantly favored at saturation. The presence of $(2 \times 2)$ structures is likely due to kinetic limitations resulting in $\theta_0$ asymptotically approaching 0.5 ML. Formation of oxygen overlayers is the result of $O_2$ dissociatively adsorbing on the Rh(111) surface. On clean Rh(111), O adatoms first form the $(2 \times 2)$ adlayer to reach $\theta_0 = 0.25$ ML. As further O accumulates, the $(2 \times 1)$ structure forms to accommodate the higher O coverage. The AES and TPD data suggest that the probability for dissociative adsorption remains high as $\theta_0$ passes 0.25 ML and uptake only slows significantly once $\theta_0$ nears 0.5 ML. This suggests that $O_2$ readily adsorbs within $(2 \times 2)$ domains. At the same time, previous authors have found that $(2 \times 2)$ structures coalesce into islands which grow to cover the surface before $(2 \times 1)$ structures develop.$^{53,50}$ This, combined with the fact that the surface saturates after forming $(2 \times 1)$ structures, suggests that the O atoms needed to form the higher coverage $(2 \times 1)$ structures are due to $O_2$ dissociation within $(2 \times 2)$ domains. Unlike the $(2 \times 1)$ structure, the $(2 \times 2)$ structure has adjacent fcc sites where O atoms can adsorb. STM images did not show any evidence of isolated $(2 \times 1)$ structures forming within $(2 \times 2)$ domains. Therefore, it appears that O atoms move to the edges of the $(2 \times 2)$ islands after dissociating and that the transformation between structures occurs near domain boundaries.

Generation of O atoms within $(2 \times 2)$ structures followed by transformation to $(2 \times 1)$ structures at the edge of domains would explain the persistence of small $(2 \times 2)$ domains and the asymptotic approach to 0.5 ML coverage. The probability of an $O_2$
molecule adsorbing within a (2 × 2) island decreases as more of the surface is covered by (2 × 1) structures. The ratio of the area within the domains where O atoms are generated to the edge of the domains where conversion occurs also decreases. This suggests that small islands will continue to coexist with the higher coverage (2 × 1) structure even after extended dosing.

Although dosing Rh(111) with O\textsubscript{2} under UHV conditions results in a maximum $\theta_{\text{O}}$ of 0.5 ML, higher coverages have been observed. O\textsubscript{2} has a very high sticking probability for dissociative adsorption at temperatures above 110 K, but dissociation requires adjacent vacant fcc sites. The probability of dissociative adsorption drops with increasing $\theta_{\text{O}}$. Coverages above 0.5 ML are thermodynamically possible but are kinetically unlikely from the dissociation of O\textsubscript{2} on the surface.$^{61}$ When the surface is exposed to elevated O\textsubscript{2} pressures or gas-phase oxygen atoms, coverages over half a monolayer have been observed.$^{59,61,62,19}$ Kohler et al. observed (2√3 × 2√3)R30° and (2 × 2)-3O structures after exposing Rh(111) to 1.3 × 10^{-3} mbar O\textsubscript{2} at 400 K for 300 s.$^{19}$ The calculated $\theta_{\text{O}}$ for the two structures was 0.66 and 0.75 ML respectively. Unlike previously observed Rh(111)/O structures in which oxygen adsorbs only to fcc sites, oxygen also adsorbs to hcp sites in the proposed (2√3 × 2√3)R30° and (2 × 2)-3O structures. Adsorption in hcp sites was found to be stable due to relaxation in the structure induced by the high coverage. The (2√3 × 2√3)R30° is shown in Figure 27 (A). There are 8 oxygen atoms per unit cell, 6 in fcc sites and 2 in hcp sites. DFT calculations by Kohler et al. showed that the structures were less stable than both surface and bulk oxide phases. However, the oxides were kinetically hindered, and only formed at higher pressures or temperature > 800 K.
Figure 27. Models of higher coverage O structures on Rh(111). (A) $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure. Overlay shows unit cell containing 6 O atoms on fcc sites and 2 O atoms on hcp sites. (B) $(1 \times 1)$-O structure. Gray balls are Rh surface atoms. Red balls are O atoms on fcc surface sites and orange balls are O atoms on hcp surface sites.

With atomic rather molecular oxygen, Sibener and co-workers also produced a $\theta_O$ of $> 0.5$ ML on Rh(111). Using He diffraction, they identified $(1 \times 1)$ surface structures. TPD experiments showed that desorption of higher than the equivalent of 1.0 ML of O$_2$ was possible without disruption of the $(1 \times 1)$ structure. Based on the combination of He diffraction and TPD, they were able to conclude that oxygen was absorbed into the bulk, and that the absorption into the bulk was facilitated by the $(1 \times 1)$ surface. Sibener et al. were also able to produce $(1 \times 1)$ surface structures on Rh(111) using NO$_2$.

While previous reports have shown that subsurface O absorption is facilitated by the $(1 \times 1)$ structure at $\theta_O \geq 1.0$ ML, high surface coverage may not be required for absorption. Wider et al. showed that at elevated temperatures and high O$_2$ exposures, O absorbs into the subsurface despite the persistence of the $(2 \times 1)$ overlayer. After exposure to $10^5$ L of O$_2$ at 470 K, they found small amounts of oxygen occupied subsurface octahedral sites. In addition, they found that the presence of subsurface O
forced O atoms in fcc surface sites above the embedded O to switch to hcp sites. A similar result has been observed on Pt(111), which is known to saturate at $\theta_O = 0.5$ ML with a $(2 \times 2)$ surface structure. Using TPD, Bashlakov et al. showed that dosing a Pt(111) surface at a sample temperature of 400-600 K yielded $\theta_O > 0.5$ ML. STM imaging of the surface showed that despite the increased oxygen, the $(2 \times 2)$-O surface structure remained intact. In addition to AO exposure and high temperature exposure of O$_2$, it is possible that surface defects, such as step edges, enhance absorption of oxygen atoms into the subsurface.

Regardless of how O is absorbed by Rh, it is clear that the total amount of O present can exceed the terminal coverage of the surface, whether that is 0.5 ML for the $(2 \times 1)$ structure or 1.0 ML for the $(1 \times 1)$ adlayer. Combining TPD and STM studies allows both surface and subsurface oxygen to be investigated. This approach was used to clarify the nature of the surface structures after AO dosing and to quantify the formation of subsurface O. AO was generated by thermally cracking molecular O$_2$ over a hot Ir filament using the method detailed in Chapter 2. The front face of the Rh(111) sample was brought to within 0.5 cm of the Ir filament, and the chamber was backfilled with $5.0 \times 10^{-7}$ Torr O$_2$. O$_2$ was continuously introduced through a leak valve and the chamber was pumped by a TMP, allowing a constant flow of O$_2$ while maintaining a stable pressure in the chamber. The Ir filament was powered by AC current, heating it to $\approx 1,750$ K. The sample was held at 320 K, the same temperature used for the O$_2$ trials. As with the O$_2$ dose, the sample was heated at a rate of 4 K$s^{-1}$ by a combination of radiative and e$^-$ beam heating for the TPD measurements.
Figure 28. TPD spectra after AO and O$_2$ dosing on Rh(111). The graph shows desorption of various O coverages from 0.25 to 2.2 ML. O$_2$ exposure reaches a terminal coverage indicated by the 30 L (black). Exposure to AO deposits O both on the surface and in the subsurface, resulting in $\theta_O$ values up to 2.2 ML.

The TPD data in Figure 28 show representative desorption spectra after the surface was dosed with AO. The O$_2$ TPD spectra after exposure of Rh(111) to AO resulted in a sharp, well-defined peak above 800 K as well as a broad feature extending past 1,300 K. The broad desorption peak corresponds to desorption from a surface with $\theta_O \leq 0.5$ ML coverage.$^{49,59}$ The sharp peak near 800 K, seen after AO exposure with total $\theta_O > 0.5$ ML, could be due to desorption from the (1 × 1) structure. However, the amount of oxygen desorbing is not consistent with a single surface layer. Figure 29 shows the integrated desorption yield of O$_2$ after exposure of Rh(111) to AO (red squares) and O$_2$ (black squares). Comparing the curves shows that AO exposure readily yields $\theta_O$ not only > 0.5 ML, but also well over 1.0 ML. Therefore, while some O$_2$ desorption likely does come from high coverage structures such as (1 × 1), another source of O must be present.
Figure 29. Plots of integrated areas of TPD spectra. O\textsubscript{2} dosing (black squares) quickly saturates the surface but does not lead to O\textsubscript{sub} formation. As a result, the integrated TPD area plateaus. With AO dosing (red squares), the integrated TPD area continues to grow resulting in significantly more than the equivalent of 1.0 ML.

The most likely explanation for the sharp peak near 800 K is subsurface O. In addition to the fact that more than the equivalent of 1.0 ML of O\textsubscript{2} desorbs, the assignment is supported by the apparent zero order shape of the peak. A common leading edge with the peak maximum shifting to higher temperatures is characteristic of zero order desorption kinetics.

The sharp drop after the peak maximum is also characteristic of zero order desorption, which is typically associated with multilayer coverage. With multilayer coverage, desorption still only occurs from the top layer. Regardless of whether a sample has 5 or 10 layers, for example, the onset of desorption will begin at the same temperature because the top layer is essentially the same in each case. The peak height, which represents the rate of desorption, will continue to increase due to the linear temperature ramp. The temperature increases as each succeeding layer is exposed, so
each layer desorbs more rapidly than the preceding layer. Once the bottom layer desorbs, the peak drops sharply because the supply of adsorbates has been exhausted.

An analogous process for subsurface species desorbing from the surface results in a similar TPD peak. However, because oxygen desorbs as a molecular rather than atomic species from Rh(111), recombination must take place so true zero order desorption is not possible. Typically, recombinative desorption shows 2\textsuperscript{nd} order desorption kinetics. A common trailing edge with the peak maximum shifting to lower temperatures is characteristic of 2\textsuperscript{nd} order desorption.\textsuperscript{113} Looking at Figure 28, the curves for desorption from the (2 × 1) structures are consistent with 2\textsuperscript{nd} order desorption. After the initial sharp peak near 800 K, the curves for AO doses greater than \( \theta_O > 0.5 \) ML are essentially identical to curves from (2 × 1) structures resulting from O\textsubscript{2} dosing. This implies that after the initial desorption of oxygen, the surface retains a similar structure to that found after O\textsubscript{2} dosing. The most likely explanation for the shape of the two peaks is that desorption of oxygen for \( \theta_O > 0.5 \) ML has pseudo zero order kinetics.\textsuperscript{139} Recombinative desorption leading to pseudo zero order peaks has been reported for other surfaces.\textsuperscript{140} In the present case, the emergence of oxygen from the subsurface is a zero order process that does not depend on coverage. Emergent O atoms from the subsurface may transiently adsorb into an unstable hcp surface site, but they will rapidly react with O\textsubscript{ad} in fcc sites or other emergent O atoms, resulting in rapid desorption of O\textsubscript{2} until the subsurface is depleted. This analysis is further supported by a closer examination of the shape of the AO peaks in Figure 28. Although there is a rapid drop after \( T_{\text{max}} \), the peak is slightly rounded, particularly for lower coverages. The fact that the AO spectra after the initial peak mirrors desorption of less than 0.5 ML of (2 × 1) suggests that some of the surface
structures are being depleted. $T_{\text{max}}$, which should coincide with the depletion of subsurface O, occurs at a lower temperature for lower coverage. At lower temperatures, emergent O atoms have less energy, move less quickly on the surface, and take longer to recombine. Consequently, for lower coverages a more gradual decrease in the rate of desorption after $T_{\text{max}}$ would be expected.

Figure 30. STM image of (2 × 1) structure after 40 s AO dose. Image of the Rh(111) surface after dosing with AO at 320 K for 40 s to give an effective $\theta_0 = 1.1$ ML. $T_s = 80$ K, $I_T = 160$ pA, $V_b = 620$ mV.

STM imaging was used to further clarify the surface structures formed after AO dosing. Figure 30 shows an STM image taken after the surface was dosed with AO for 40s. TPD analysis showed that 40 s AO doses resulted in the accumulation of the equivalent of 1.1 ML of oxygen. Figure 30 shows that the striped pattern that was observed after $O_2$ dosing was still present after AO dosing. Images clearly showed that
despite the high coverage, (2 × 1) structures were still present on the surface. These areas typically had more defects than similar areas found after O₂ dosing, but still clearly exhibited the (2 × 1) adlayer structure. Surface lattice vectors were determined to be 5.50 ± 0.17 Å by 2.56 ± 0.21 Å, essentially the same as the spacing seen after dosing with O₂.

Figure 31. STM image of (2 × 1) and (2 × 2) structures. Domains of (2 × 2) (left) and (2 × 1) (right) and their boundary are clearly resolved. Ts = 80 K, I₉ = 160 pA, V₉ = 0.62 V.

While (2 × 1) structures were most prevalent, other structures were also observed. STM imaging revealed that even when θ₀ > 1.0 ML, (2 × 2) domains were still present. Figure 31 shows an image of a boundary between (2 × 1) and (2 × 2) domains running vertically near the left side of the image. Figure 32 shows a close up of the (2 × 2) structure.
Figure 32. STM image of (2 × 2) domain on Rh(111). $\theta_O = 0.6$ ML after dosing with AO at 320 K. $T_s = 80$ K, $I_T = 160$ pA. $V_b = 0.62$ V.

Although the presence of (2 × 1) and (2 × 2) domains was similar to results obtained after O$_2$ dosing, there were also significant differences after AO dosing. When the surface was dosed with AO to reach O coverages of 0.6 ML, STM images showed bright islands several nanometers in diameter. The islands were most commonly found along step edges. Figure 33 shows (2 × 1) domains near a terrace step edge that runs along the bottom of the image. The bright islands along the step edge have a hexagonal lattice structure that is half the size of the (2 × 2) structures which were observed. The spacing of the observed lattice was measured to be $2.50 \pm 0.17$ Å by $2.50 \pm 0.17$ Å. These values are in agreement with the reported Rh(111) in-plane spacing of 2.69 Å that would be expected for a (1 × 1) structure.$^{12}$
Figure 33. STM image of (2 × 1) domains and (1 × 1) islands. Image taken after AO exposure for 25 s at 320 K. Two (2 × 1) domains offset by 60° meet near the top of the image. The bright areas near the bottom are (1 × 1) islands. T_s = 80 K, I_T = 230 pA, V_b = 0.62 V.

Figure 34. STM image of (1 × 1) island. Enlargement of (1 × 1) island in Figure 33 shows the hexagonal structure. T_s = 80 K, I_T = 230 pA, V_b = 0.62 V.

When the surface was exposed to longer doses of atomic O, the (1 × 1) islands became larger and comprised a greater portion of the surface. However, even after longer
doses, the surface was principally (2 × 1) domains. Figure 35 shows an area of the Rh(111) surface after exposure to AO and a total oxygen coverage of $\theta_O = 1.1$ ML, as determined from TPD measurements. The image shows that the (1 × 1) domain is larger but a (2 × 1) domain is still present.

Figure 35. STM image of large (1 × 1) domain. Despite the high total amount of O leading to a large (1 × 1) domain, a (2 × 1) domains is visible on the right part of the image. The white line drawn on the image shows the domain boundary. $T_s = 80$ K, $I_T = 160$ pA, $V_b = 0.62$ V.

This is in agreement with the interpretation that after exposure to AO, (1 × 1) surface structures form sparingly about the Rh surface. Island formation appears to be favored on step edges, rather than as a uniform structure covering the majority of the Rh surface. Instead of becoming bound to the surface, the majority of impinging oxygen atoms penetrate into the subsurface, where they are stably embedded. These coverages (up to 1.3 ML) are significantly lower than those required for formation of surface oxides. Figure 36 shows the surface after dosing with AO yielding the equivalent of 1.3 ML of oxygen. Significantly more adatoms and defects are present, but the stripe pattern
of the (2 × 1) structure is still present. Figure 37 shows another area of the surface after the same dose. Both (2 × 1) and (2 × 2) domains are visible in the image. (2 × 1) domains can be seen on the bottom of Figure 37 while a (2 × 2) is visible at the top. While the lower coverage structures remained despite doses equivalent to 1.3 ML, the high coverage (2√3 × 2√3)R30° structure reported by Kohler et al. was not seen.19 The √3 × √3 structure of Rh$_2$O$_3$(0001), as well as a larger (9 × 9) Moiré pattern characteristic of a Rh–O–Rh trilayer, were also not observed.141

Figure 36. STM image after extended AO dosing of large (1 × 1) domain. Image was taken after 60 s AO dose, equivalent to 1.3 ML of O. Significantly more adatoms and clusters are visible on the surface, but the (2 × 1) structure is still present. T$_s$ = 80 K, I$_T$ = 160 pA, V$_b$ = 0.62 V.
Figure 37. STM image showing (2 × 1) and (2 × 2) domains. Image was taken after AO dose yielding 1.3 ML of O. The bottom of the image shows (2 × 1) domains and the top shows a (2 × 2) domain. $T_s = 80$ K, $I_T = 160$ pA, $V_b = 0.62$ V.

At total oxygen coverages greater than 1.3 ML, it is possible that the oxide would be observed, although elevated temperatures may be required. Because significant areas of the surface were covered by the (2 × 1) and (2 × 2) structures rather than the high coverage (1 × 1) structure previously observed to be the source of the sharp O$_2$ TPD desorption peak near 800 K, the present observations suggest that emerging subsurface oxygen is the most significant source of the observed O$_2$ desorption. The sharp TPD peak at 800 K also suggests that when the total amount of O present exceeds 0.5 ML, the oxygen–oxygen repulsion dominates. Emerging oxygen rapidly desorbs rather than remaining on the surface. The STM images clearly show that the surface is not uniformly covered with domains in which $\theta_o > 0.5$ ML. Therefore, all of the oxygen is not present...
on the surface, and some must be in the subsurface. Unlike the atomic-beam study by Gibson et al., a uniform (1 × 1) surface structure is not the dominant surface structure responsible for the sharp desorption peak at 800 K.\textsuperscript{59} It is more likely that the small (1 × 1) domains, seen at $\theta_O \geq 0.6$ ML, facilitate O incorporation into the subsurface. In the TPD experiments, the O atoms emerge from the subsurface before appreciable desorption from the (2 × 1) adlayer. This suggests $O_{sub}$ is metastable with respect to $O_{ad}$ and that the (2 × 1) structure is the thermodynamically favored surface from 300 to 1,300 K.

Although the Gibson et al. results clearly demonstrated that an O atomic beam can grow large domains of (1 × 1), when the flux of O atoms was increased, the quality of the domains decreased.\textsuperscript{142} It is likely that the hot filament O atom source used here generated a significantly higher flux, as indicated by the shorter dose times to reach $\theta_O = 1$ ML. The higher flux of O atoms disfavors the (1 × 1) structure in favor of filling the subsurface. Finally, the translational energies of O atoms from the two sources differ. The atomic beam generates a beam of O atoms in the ground electronic state with a narrow kinetic energy distribution.\textsuperscript{143} On the other hand, dissociation over the hot filament likely generates a host of metastable oxygen species in addition to O atoms. Additionally, oxygen atoms from the hot filament likely have an average translational energy around 430 meV, corresponding to the temperature of the Ir filament. The O atom beam’s average translational energy was only 60 meV. It is reasonable that differing energies of the incident oxygen atoms affected the nature of the structures formed and the likelihood of uptake into the subsurface.

TPD measurements showed that the Rh(111) surface is capable of the uptake of a significant amount of oxygen, at least the equivalent of 2 ML. STM images showed that
despite the presence of O in excess of the equivalent of 1.0 ML, surface structures were not drastically altered from the stable structures formed by the dissociative adsorption of O$_2$. The combination of stable oxygen adlayers and energetic impinging oxygen atoms greatly facilitates the uptake of oxygen into the subsurface. The ability of STM to determine surface structures for well-defined O coverages was used to show that at high total coverages of oxygen on Rh(111) not all oxygen was bound to the surface. The stable (2 × 1) structures formed at 0.5 ML persisted while islands of (1 × 1) formed along surface defects. The efficacy of atomic oxygen incorporation into the subsurface likely depends on both the energy of the incident O atoms and the nature of the Rh surface. These results show that even under low pressure and modest temperature conditions, several surface phases coexist and subsurface oxygen accumulation is possible.
CHAPTER FOUR

SOURCE EFFECTS ON THE ADSORPTION AND ABSORPTION OF OXYGEN ON AG(111)

At high temperatures and pressures, the surfaces of catalytically active transition metals have been shown to be highly dynamic.\textsuperscript{9,11} This project addressed the challenge of using UHV techniques, including TPD and STM, on catalytically relevant structures by using AO to create high coverage O/Ag structures on Ag(111). The practical and theoretical importance of the interaction of oxygen with transition metal surfaces has generated significant research for many years.\textsuperscript{144-147} The interaction of Ag with O has been one of the most widely studied and debated systems.\textsuperscript{83} Research interest in the Ag/O system has been motivated mainly by silver's importance as the partial oxidation catalyst, particularly in the production of ethylene oxide from ethylene.\textsuperscript{148}

Oxygen induced reconstructions of the Ag surface have been studied intensely since the 1970s, and a variety of models were proposed and ultimately dismissed before the currently accepted model was developed.\textsuperscript{149} The present model of the $p(4 \times 4)$-O/Ag(111) structure consists of two triangles containing six Ag atoms each, separated by a furrow containing two O atoms. This model has been supported by subsequent studies. Two other similar oxygen surface structures on Ag(111) have also been identified: a $c(3 \times 5\sqrt{3})$ structure composed of the same six Ag atom triangles, but arranged differently, and a $p(4\times5\sqrt{3})$ structure which contains two triangles consisting of 10 Ag atoms.\textsuperscript{65}
Models of the structures are shown in Figure 38. Many additional structures, including a \( p(4 \times 8) \) structure found by Schnadt et al.\(^8\) and a bulk-like \( \text{Ag}_2\text{O}(111) \) oxide resulting in a \( p(7 \times 7) \) reconstruction, have also been reported.\(^6\)

![Figure 38. Models of O/Ag(111) structures. (A) \( p(4 \times 4) \); (B) \( c(3 \times 5\sqrt{3}) \); (C) \( p(4 \times 5\sqrt{3}) \). Unit cells are shown for each model. Light grey balls are substrate Ag atoms, darker grey balls are Ag atoms in overlayer, and red balls are O atoms.](image)

One of the challenges in studying O/Ag(111) structures using UHV based surface science methods is the low sticking probability of \( \text{O}_2 \) on Ag(111). Although Ag readily oxidizes at atmospheric or elevated pressures, the sticking probability of \( \text{O}_2 \) on Ag(111) at 300 K is \( \approx 1.0 \times 10^{-6} \).\(^7\) This has led to a wide variety of approaches to oxidize Ag. Many initial experiments relied on elevated pressure \( \text{O}_2 \) dosing. \( \text{NO}_2 \) has also been used by several groups to produce \( p(4 \times 4) \)-O structures.\(^34,150\) Other approaches have included \( \text{O}_3 \) and atomic oxygen.\(^151\) In addition to the variety of dosing methods that have been used to study the oxidation of Ag(111), a wide range of sample temperatures have been used. There have been a handful of studies on the interaction of oxygen with Ag at cryogenic temperatures.\(^152,153\) Other studies have looked at oxidation at higher temperatures.\(^154\) However, the majority of research done on O/Ag(111) system has focused on temperatures around 500 K. One reason researchers have focused on this temperature range is because it is near the temperature at which Ag catalyzed EO
synthesis is carried out. It is also only slightly below the temperature at which the $p(4 \times 4)$ structure desorbs.

In order to investigate the effect of atomic oxygen flux and energy on surface structure formation and subsurface oxygen absorption, the sample was dosed with atomic oxygen at 500 K for this project. TPD, AES, and STM experiments were done after dosing an Ag(111) sample with AO generated using an Ir filament at two different temperatures. At the lower temperature setting, the filament temperature ($T_{\text{fil}}$) was $\approx 1,750$ K. At the higher temperature setting, $T_{\text{fil}}$ was $\approx 2,000$ K. All other dosing conditions were kept the same in an effort to isolate and study the effects of AO energy and flux.

The Ag(111) crystal (Surface Preparation Laboratory) was 1.5 mm thick and 10 mm $\times$ 6 mm. The crystal was initially cleaned by repeated cycles of Ar+ sputtering at room temperature followed by annealing for 10 min at 750 K. Cycles were repeated until surface impurities were below the detection of the AES. Surface cleanliness was also confirmed by LEED, TPD and STM imaging. Figure 39 shows a LEED image and AES spectra taken after cleaning. Between trials, the crystal was again cleaned by Ar+ sputtering for 5 min followed by annealing for 5 min at 750 K.

Figure 39. LEED and AES of clean Ag(111). The LEED image was taken at 62 eV and shows a hexagon of sharp spots indicating a clean (111) surface. The AES spectra shows only Ag and does not show any peaks indicating surface contaminates.
Atomic oxygen was generated by dissociating O\textsubscript{2} over a hot Ir filament using the method described in Chapter 2. For most of the trials, the chamber was backfilled with 5.0 × 10\textsuperscript{-7} Torr of O\textsubscript{2}. For some trials, a higher or lower O\textsubscript{2} pressure was used to investigate the effect of O flux. O\textsubscript{2} was continuously introduced through a leak valve and the chamber was pumped by a TMP, allowing a constant flow of O\textsubscript{2} while maintaining a stable pressure in the chamber. The sample was held at 500 K during all of the dosing for this project. During dosing, even when the higher filament power was used to dissociate O\textsubscript{2}, the sample temperature remained stable. For TPD experiments, the sample was cooled to 400 K immediately after dosing. A temperature ramp of 3 K s\textsuperscript{-1} was used for all TPD trials. STM images were obtained at 80 K using Pt/Ir tips fabricated by the method described in Chapter 2.

Figure 40. TPD spectra after AO dosing with lower T\textsubscript{fil}. After dosing, the sample was cooled to 400 K and the then temperature was ramped to 1,000 K at 3 K s\textsuperscript{-1}. After short doses, a small peak forms near 600 K. For longer doses, a second lower temperature peak forms. After extended dosing, the lower temperature peak overlaps the initial peak.
Figure 40 shows TPD spectra recorded after dosing the Ag(111) crystal with various amounts of AO with $T_{\text{fil}} = 1,750$ K. Initially, a small peak is seen at 600 K. With longer exposure, a second peak forms with a $T_{\text{max}}$ of $\approx580$ K. The lower temperature peak continues to grow with increasing exposure, eventually overlapping the higher temperature peak. Previous authors have assigned the higher temperature peak to randomly chemisorbed O adatoms and the lower peak to surface oxides.\textsuperscript{34,150} However, the assignment of peaks in this region only to surface species was based on studies conducted with NO$_2$, which does not yield subsurface oxygen. In the present case, the peak does not show evidence of saturation, suggesting that there is a significant contribution from subsurface oxygen. In the TPD spectra in Figure 40, a broad peak between 700 K and 800 K is also visible. The peak was always significantly smaller than the primary desorption peak, and appeared to saturate after 5 min exposure. The peak is attributed to the decomposition of small amounts of stoichiometric Ag$_2$O oxide on the Ag(111).\textsuperscript{157}

Atomic oxygen not only adsorbs to metal surfaces, but also penetrates the surface to form subsurface oxygen.\textsuperscript{66,158} On Ag(111), O$_{\text{sub}}$ can reemerge from the bulk at elevated temperatures and recombinatively desorb as O$_2$. Therefore, the O$_2$ desorption peak in the TPD experiments quantifies the total amount of oxygen, both adsorbed and subsurface. AES is sensitive only to O on or near the surface, so AES was used to determine the surface coverage. Figure 41 (blue line) shows a plot of the ratio of 503 eV oxygen peak to the 353 eV Ag signal after dosing with AO generated with the filament at lower power. Looking at the graph, it is clear that while the integrated area of the TPD continues to increase, the ratio of the AES signals quickly saturates. The fact that the surface
coverage, determined by the AES ratio, is constant while the total amount of O increases suggests that O is being absorbed into the subsurface.

Figure 41. Plot of AES signal ratio after AO dosing. The ratio of 503 eV oxygen AES signal to 353 eV Ag signal after various AO doses is plotted against the integrated O$_2$ TPD area for both high (red) and low (blue) filament power. With the lower T$_{fil}$, the signal quickly saturates. With the higher T$_{fil}$, the total amount of O$_2$ desorbing increases slowly, but the ratio of AES signals continues to increase.

Figure 42 shows TPD spectra after exposure of Ag(111) to AO with T$_{fil}$ = 2,000 K. In contrast to the results with the lower T$_{fil}$, with the high T$_{fil}$ the primary desorption peak is now close to 800 K and the T$_{max}$ shifts higher with increasing coverage. The smaller peak near 600 K appears to saturate after 5 minutes of AO exposure. The position of the smaller peak is consistent with the peak observed after dosing with the lower T$_{fil}$. The striking difference between the TPD spectra for T$_{fil}$ = 1,750 K and 2,000 K is that the intensity of the two O$_2$ desorption peaks have switched. TPD spectra show that both peaks are present after longer deposition at either T$_{fil}$, but the proportion of each changes
substantially based on $T_{\text{fil}}$. The higher desorption temperature resulting from dosing with the higher $T_{\text{fil}}$ also implies that oxygen is more tightly bound to the surface.

Figure 42. TPD spectra after AO dosing with higher $T_{\text{fil}}$. After dosing, the sample was cooled to 400 K and the then temperature was ramped to 1,000 K at 3 K s$^{-1}$. With the higher $T_{\text{fil}}$, a high temperature desorption peak forms with an initial $T_{\text{max}}$ near 750 K. With longer doses, the lower temperature peak remains the same, but the high temperature peak continues to grow.

Figure 43 highlights the difference in the TPD data due to $T_{\text{fil}}$. Doses from 1 to 5 min are shown for both $T_{\text{fil}}$. The difference between the two filament settings is clear from the onset of dosing. For short doses with the low $T_{\text{fil}}$, the higher temperature peak near 800 K is not present. Even by the 1 minute dose, the peak associated with $O_{\text{sub}}$ is most prominent. After short doses with the high $T_{\text{fil}}$, the low and high temperature desorption peaks are present. However, the lower temperature peak is not a double peak, and there is no evidence of $O_{\text{sub}}$ desorption. For doses ≤ 2 min with the high $T_{\text{fil}}$, the high and low temperature peaks are nearly the same height, but for the 5 min dose, only the high temperature peak increases.
The kinetic order of the low temperature desorption peak is complicated by the overlap of two peaks. Once the second peak begins to grow, the leading edges line up and $T_{\text{max}}$ increases with $\theta_O$. This is consistent with zero order kinetics and suggests a pseudo zero order model analogous to subsurface O emerging on Rh(111). Atomic O emerging from the bulk is a zero order process, which is followed by rapid recombination on the surface. The high temperature peak also involves recombinative desorption, but it also does not display any second order characteristics. For low the low $\theta_O$ shown in Figure 43, the peak appears to be first order. A similar result was seen by with O$_2$ desorption from Au(111). In that case, the authors concluded that the rate limiting step in the desorption process was the conversion of oxidic O into chemisorbed O, rather than the recombination of O$_2$. A similar process likely explains the first order peak observed here for low coverages. This is supported by the high coverage TPD data in Figure 40. At higher $\theta_O$, the high temperature peak has a common leading edge and $T_{\text{max}}$ increases with
coverage, typical for zero order desorption, which would be expected for multilayer desorption of a first order process.

The existence of lower and higher temperature O\textsubscript{2} desorption peaks on Ag has been previously reported, but only under substantially different conditions. Ertl and coworkers observed two TPD peaks, one at 600 K and one just above 900 K, after exposing polycrystalline Ag to 10 mbar O\textsubscript{2} for 5 min at 520 K.\textsuperscript{158} Bowker et al. observed a lower temperature peak near 560 K as well as a high temperature peak near 850 K using Ag powder.\textsuperscript{160} They exposed the sample to 6.0 \times 10^{4} L O\textsubscript{2} at 453 K and then ramped the temperature up to 720 K to obtain TPD data. The process was repeated three times, and then after a fourth dose, a peak was observed at 850 K when a TPD was run up to 920 K. Schlogl and coworkers were able to identify an oxygen species stable up to 900 K on Ag(111).\textsuperscript{161} However, to produce the species they needed to expose the crystal to 1 bar of O\textsubscript{2} at 780 K for 1 h. They concluded that the (111) crystal face had been transformed to a polycrystalline surface due to oxygen induced faceting. Oxygen interacts differently, and has very different sticking probabilities, on different faces of Ag crystals. For example, at 300 K, the dissociative sticking probability of O\textsubscript{2} is \approx1.0 \times 10^{-3} on Ag(110) and 4.4 \times 10^{-3} on Ag(100) compared to \approx10^{-6} on Ag(111).\textsuperscript{162,163} It is notable here that similar behavior is observed from changing the gas-phase species, even after short doses without changes in the surface temperature or changes in the background pressure. Furthermore, the crystal was not irreversibly changed by dosing with the higher temperature filament. Standard sputtering and annealing cycles between trials was sufficient to restore the crystal surface.
Figure 44. Comparison of surface coverage and total abundance of oxygen. (A) AES data shows more rapid surface uptake for the 2,000 K temperature. (B) Integrated TPD peak areas show that initial uptake is greater, but diminishes with exposure for the hotter filament, whereas uptake linearly increases with the lower filament temperature.

Figure 44 A) shows $\theta_O$ for both filament settings and Figure 44 B) shows the integrated area of the corresponding TPD spectra. For both deposition conditions, the initial uptake of $O_{ad}$ is rapid, but the initial uptake for $T_{fil} = 2,000$ K is about 2.5 times more than for $T_{fil} = 1,750$ K. As the exposure time increases, their behaviors continue to diverge. As mentioned, $\theta_O$ saturates after 5 minutes of AO exposure with $T_{fil} = 1,750$ K. In comparison, for $T_{fil} = 2,000$ K, $\theta_O$ continues to increase, albeit more slowly. The trend in the TPD data is different. The total uptake of O is initially similar for both dose conditions, with a slightly greater uptake for $T_{fil} = 2,000$ K. However, while the TPD integral continues to increase linearly for $T_{fil} = 1,750$ K, the uptake appears to diminish for $T_{fil} = 2,000$ K. This implies that with the hotter filament, less O is sticking. Also, the O that does stick with the hotter filament is on or very near the surface. In comparison, at $T_{fil} = 1,750$ K, $\theta_O$ saturates after 5 minutes of dosing. Despite the surface being saturated, O continues to accumulate. Because $\theta_O$ is not increasing, the additional O must be in the
subsurface. These results suggest that dramatically different surfaces form as a result of the two deposition conditions.

Figure 45. STM image of Ag(111) after 30 s AO dose. The arrow points to one of the bands of defects which run perpendicular to the main structure. Sample temperature was 500 K. $T_s = 80$ K, $I_T = 200$ pA, $V_b = 1.0$ V.

STM images were taken after AO dosing for both deposition conditions to determine how the resultant surface structures differ. With $T_{fil} = 1,750$ K, the surface structures observed were consistent with those previously reported. Figure 45 shows an image of the surface after dosing with 30 s of AO at 500 K. A single step edge is visible across the image about ¼ from the top and multiple steps edges are visible in the lower left. Overlayer structures cover almost the entire surface, extending from the base of the step edges and across the terrace, ending just before the next step edge. Large areas of the surface were covered in the $p(4\times5\sqrt{3})$. There were also bands of $c(3 \times 5\sqrt{3})$ defects
stretching across the terraces. One of the defect bands is highlighted by the gray arrow in Figure 45.

![STM image after 30 s AO dose showing screw dislocation. The overlayer extends all of the way to the step edge below the screw dislocation, but stops short at the screw dislocation and along the other step edge. $T_s = 80$ K, $I_T = 200$ pA, $V_b = 1.0$ V.](image)

Figure 46. STM image after 30 s AO dose showing screw dislocation. The overlayer extends all of the way to the step edge below the screw dislocation, but stops short at the screw dislocation and along the other step edge. $T_s = 80$ K, $I_T = 200$ pA, $V_b = 1.0$ V.

Figure 46 also shows the surface after a 30 s AO dose at 500 K. The same structure is visible across the surface. A screw dislocation can be seen in the center of the image. The overlayer structure was observed to always go to the base of step edges. Depending on the spacing of the structure, it sometimes stopped short of step edges, as seen on the step edge in the low left, or ended at the step edge, as seen on the step edge below the screw dislocation.

The predominate surface structure after dosing with AO for 30 s at 500 K was the $p(4 \times 5\sqrt{3})$ structure. Figure 47 shows a detailed image of the $p(4 \times 5\sqrt{3})$ structure and the
model proposed by Schandt et al.\textsuperscript{82} Oxygen is known to reduce the LDOS on metal surfaces. The apparent height of features in a constant current STM image is a convolution of height and the LDOS.\textsuperscript{164} As a result, O atoms generally appear as dark depressions on transition metals.\textsuperscript{165} Conversely, Ag atoms further away from O atoms generally appear brighter. The larger bright triangles in the image are the 10 Ag atom triangles. In the STM images, they are prominent not because they are higher than the six atom triangles, but their LDOS is less affected by O atoms. Oxygen atoms are present in the furrows between the triangles, but are not visible due to the decreased LDOS. The darkest circles, highlighted by arrows, are where an Ag atom is absent in the top layer.

Figure 47. STM image and model of $p(4 \times 5\sqrt{3})$ structure. The image on the left was taken after a 30 s AO dose. The rectangle depicts the unit cell. The arrows point where an Ag atom is missing from the topmost layer. $T_s = 80$ K, $I_T = 200$ pA, $V_b = 1.0$ V.

Due to the six fold symmetry of the (111) surface, the $p(4 \times 5\sqrt{3})$ structure can be oriented along three different axes, each rotated by 60°. Figure 48 shows two domains meeting at a step edge which runs vertically through the image. Along the step edge, just
above the middle of the image, an area of bare Ag is visible. The dark spots on the bare Ag are most likely chemisorbed O atoms.

Figure 48. STM image of $p(4 \times 5\sqrt{3})$ structures at step edge. A small path of bare Ag is visible along the step edge. Image taken after 30 s AO dose. $T_s = 80$ K, $I_T = 200$ pA, $V_b = 1.0$ V.

Figure 49. STM image of $p(4 \times 5\sqrt{3})$ domain boundary on terrace. (L) Boundary between two $p(4 \times 5\sqrt{3})$ domains. The area on the left part of the image is bare Ag. (R) Expanded view of the domain boundary. A small patch of $p(4 \times 4)$ structure fills in the gap between the domains. Image taken after 30 s AO dose. $T_s = 80$ K, $I_T = 200$ pA, $V_b = 1.0$ V.
Rotated domains also came together on terraces. Figure 49 shows a typical boundary between two $p(4 \times 5\sqrt{3})$ domains. The bright patches along the domain boundary are most likely islands of unreconstructed Ag atoms. The smaller image in Figure 49 is an expanded view of the domain boundary. A small area of $p(4 \times 4)$ fills the gap between the two domains. The area on the upper left of the larger image is unresolved bare Ag. For AO doses ≤ 2 min, similar areas were always present. The dark spots within the unresolved Ag area are chemisorbed O atoms.

Figure 50. STM image of $p(4 \times 5\sqrt{3})$ structures interrupted by defects. Two bands of $c(3 \times 5\sqrt{3})$ defects are visible going across the image. After the upper defect, the $p(4 \times 5\sqrt{3})$ structure continues along the same column. After the lower defect, the $p(4 \times 5\sqrt{3})$ pattern shifts. Image taken after 30 s AO dose. $T_e = 80$ K, $I_T = 200$ pA, $V_b = 1.0$ V.

Figure 50 shows an area of $p(4 \times 5\sqrt{3})$ structure with two bands of defects. Although large defect free $p(4 \times 5\sqrt{3})$ domains were sometimes present, domains with
bands of \( c(3 \times 5\sqrt{3}) \) structures were more common. Figure 50 shows that after the defect, the \( p(4 \times 5\sqrt{3}) \) structure can resume in the same alignment, as seen after the \( c(3 \times 5\sqrt{3}) \) band closer to the top, or shift over, as seen after the lower band. This shift was only ever observed after a defect band, not within an otherwise defect free \( p(4 \times 5\sqrt{3}) \) domain. The intermixing of different structures shown in Figures 50 suggests that the structures have very similar energy. The six and ten atom triangles appear to be basic building blocks that can be arranged in a variety of ways. However, isolated defects in the structures were rarely observed. Although the different structures were frequently intermixed within larger domains of other structures, the defects were almost always present as bands, columns or islands connected together. This suggests that even though different arrangements of the basic structures are possible, the presence of a particular structure makes the formation of additional similar structures more favorable.

STM imaging showed that varying the dose length had some effect on the surface structures which formed. For all dose lengths a variety of structures were observed, but the variation was most significant with intermediate dose lengths. Figure 51 illustrates the variation in surface structures which was typical for doses between 1 and 3 minutes. The image was recorded after dosing with AO for 2 min at 500 K. Domains consisting primarily of each of the three main surface structures are visible. Columns of \( p(4 \times 5\sqrt{3}) \) structures can be seen in the upper left portion of the image. In the upper right and bottom portions of the image, there are \( c(3 \times 5\sqrt{3}) \) domains with a large number of \( p(4 \times 5\sqrt{3}) \) bands. An almost defect free \( p(4 \times 4) \) domain is in the center of the image.
Figure 51. STM image showing multiple structures. The area in the upper left is $p(4 \times 5\sqrt{3})$. The upper right and lower parts of the images are $f c(3 \times 5\sqrt{3})$ with bands of $p(4 \times 5\sqrt{3})$. There is a $p(4 \times 4)$ domain in the center. Image taken after 2 min AO dose. $T_s = 80$ K, $I_T = 250$ pA, $V_b = 0.95$ V.

Figure 51 also illustrates that, despite being composed of the same Ag atom triangles, there are marked differences between the $c(3 \times 5\sqrt{3})$ and the $p(4 \times 4)$ structures. Even though there are bands of $p(4 \times 5\sqrt{3})$ structures running across the $c(3 \times 5\sqrt{3})$ domains at the top of the image, the $p(4 \times 4)$ domain adjacent to it is essentially defect free. For all dose lengths, $c(3 \times 5\sqrt{3})$ domains had some bands of $p(4 \times 5\sqrt{3})$ structures running across them. Figure 52 shows an example $p(4 \times 5\sqrt{3})$ bands in a $c(3 \times 5\sqrt{3})$ domain. Similar bands of defects were never observed in $p(4 \times 4)$ domains. When defects were present in $p(4 \times 4)$ domains, they formed islands or columns.
Figure 52. STM image after 3 min AO dose showing \( c(3 \times 5\sqrt{3}) \) structure. Bands of \( p(4 \times 5\sqrt{3}) \) structure are visible across the image. Image taken after 60 s AO dose. \( T_s = 80 \text{ K}, I_T = 280 \text{ pA}, V_b = 1.0 \text{ V} \).

Figure 53. STM image and model of the \( c(3 \times 5\sqrt{3}) \) structure. The image on the left was taken after a 1 min AO dose at 500 K. The rectangles depict the unit cell. \( T_s = 80 \text{ K}, I_T = 250 \text{ pA}, V_b = 1.0 \text{ V} \).
The \( p(4 \times 4) \) structure has been the most studied of the O/Ag(111) structures at least in part because it is believed to be the predominate structure when Ag(111) is exposed to high pressure \( O_2 \). While large \( p(4 \times 4) \) domains were observed after some AO doses, some \( p(4 \times 5\sqrt{3}) \) and \( c(3 \times 5\sqrt{3}) \) structures were always also present. Figure 54 shows an example of a \( p(4 \times 4) \) domain recorded after a 1 min AO dose at 500 K.

![Figure 54](image)

**Figure 54.** STM image after 1 min AO dose showing \( p(4 \times 4) \) structure. A step edge is visible across the top of the image. \( T_s = 80 \) K, \( I_T = 200 \) pA, \( V_b = 0.98 \) V.

Figure 55 shows an image of a \( p(4 \times 4) \) structure taken after a 5 minute AO dose at 500 K and the model proposed by the Besenbacher and Varga groups. The gray diamonds show the unit cell on each. Figure 56 shows an example of a typical \( p(4 \times 4) \) domain with \( p(4 \times 5\sqrt{3}) \) structures within it. The image on the right of Figure 56 is an enlargement of the area highlighted by the gray rectangle. It shows a small area of \( c(3 \times \)
$5\sqrt{3}$ formations. Under all dosing conditions, this was one of the only examples of $c(3 \times 5\sqrt{3})$ structures within a $p(4 \times 4)$ domain. Figure 51, where there was clear boundary between the $p(4 \times 4)$ and $c(3 \times 5\sqrt{3})$ domains was much more typical.

Figure 55. STM image and model of the $p(4 \times 4)$ structure. The image on the left was taken after a 5 min AO dose at 500 K. The diamonds depict the unit cell. $T_s = 80$ K, $I_T = 200$ pA, $V_b = 0.9$ V.

Figure 56. STM image of $p(4 \times 4)$ domain surrounding $p(4 \times 5\sqrt{3})$ structures. The image on the right is an enlargement of the area enclosed by the rectangle, showing a small region of $c(3 \times 5\sqrt{3})$. Image taken after 1 min AO dose. $T_s = 80$ K, $I_T = 260$ pA, $V_b = 0.9$ V.
Despite variations in the ratio of the three main O/Ag(111) structures observed after AO dosing with the lower power filament, several things were consistent. For all dose lengths, STM images showed either bare unresolved Ag terraces with O adatoms, or well-defined O/Ag(111) reconstructions. The fact that tunneling was possible on all of the surfaces supported the AES data and showed that oxygen was not accumulating at the surface and forming bulk oxides. In order to study the effect of AO energy and flux, STM was also used to look at the surface after dosing with the high temperature filament. Figure 57 shows the surface after a 90 s dose at 500 K using the high temperature filament. Although step edges running diagonally down and to the left are visible, they are no longer straight and show significant signs of degradation.

Figure 57. STM image after 90 s AO dose with high $T_{\text{fil}}$. The step edges are uneven and round depressions are visible across the surface. $T_s = 80$ K, $I_T = 200$ pA, $V_b = 0.95$ V.
With longer dosing, the disruption of the Ag(111) surface by the high $T_{fil}$ AO was even more evident. Figure 58 shows the surface after a 2 min dose. Step bunching, which is seen in the lower left part of Figure 58, was typical after dosing with the high $T_{fil}$. Just as with the 90 s dose, the step edges were highly irregular after the 120 s dose. Some of the dark areas stretched from step edge to step edge, but more often they grew along the base of step edges. After 90 s, darker areas along step edges typically stretched for 10-20 nm. Dark areas after 120 s doses stretched along the base of step edges for 50 nm or more. In addition to the expansion of the dark areas, some areas also developed hexagonal patterns. An example of a hexagonal pattern is highlighted by the gray arrow in the lower left part of Figure 55.

![Figure 58. STM image after 120 s AO dose with high $T_{fil}$. The step edges are uneven and round depressions are visible across the surface. The gray arrow points a large hexagonal pattern within one of the dark areas. $T_s = 80$ K, $I_T = 150$ pA, $V_b = 0.9$ V.](image)
Figure 59. STM image of hexagonal pattern after 120 s AO dose. The white diamond indicates the unit cell. $T_s = 80 \text{ K}$, $I_T = 200 \text{ pA}$, $V_b = 0.9 \text{ V}$.

The bright features within the hexagonal patterns were each approximately 3 nm across. The unit cell vector of the hexagonal pattern was $\approx 34.9 \text{ Å}$. This is three times the size of the unit cell vector of the $p(4 \times 4)$ structure. It is also larger than any observed or predicted O/Ag(111) reconstruction other than one predicted by Bao, et al. in an early STM investigation of oxygen on Ag(111). That study was done with atmospheric pressure O2 at 800 K, so bulk-like oxide formation was likely. The size of the hexagonal pattern suggests that it not the direct result of a new surface structure. Rather, it is consistent with a Moiré pattern resulting from a lattice mismatch between the Ag(111) and a thin bulk-like Ag$_2$O oxide.
The fraction of $O_2$ dissociated into AO is around 10-fold greater at the higher filament temperature.\textsuperscript{117} However, the initial update with the hotter filament is about twice as much for the higher $T_{\text{fil}}$. The data in Figure 44 B) shows that by 10 min, the lower $T_{\text{fil}}$ actually yields higher total O accumulation. STM images show that the nature of the surface is substantially different after dosing with the higher $T_{\text{fil}}$. This suggests that formation of the higher coverage bulk-like oxide inhibits subsurface O formation. Figure 58 shows that when dosed with the higher $T_{\text{fil}}$, only part of the surface is covered with the bulk-like oxide after 2 min. Given the increased flux due to the higher $T_{\text{fil}}$, this can be compared to dosing for 20 min at the lower $T_{\text{fil}}$. The TPD data show that after 20 min dosing with the lower $T_{\text{fil}}$ significant subsurface O is present. The amount of AO incident on the surface after dosing for 2 min with the higher $T_{\text{fil}}$ is similar to the 20 min dose with the lower $T_{\text{fil}}$ and should be sufficient to yield significant subsurface O. Because areas of bare Ag are still visible on the surface, this suggests that AO on the unreconstructed Ag surface is not sufficient for the formation of subsurface O. Further support can be seen in the TPD and AES data after dosing with the lower $T_{\text{fil}}$. A second lower temperature desorption peak is not evident until after the higher temperature peak begins to saturate.

In order to isolate the effect of AO energy from AO flux, dosing was also carried out at different pressures. As expected, the integrated area of the TPD spectra did depend on the backfilled $O_2$ pressure during dosing. The background pressure could only be increased to $1.0 \times 10^{-6}$ Torr, which was double pressure used for the other trials. At that pressure, dosing with the lower $T_{\text{fil}}$ resulted in a TPD peak with double the integrated area. However, the position of the peak was unchanged from the other lower $T_{\text{fil}}$ doses. Similarly, when the sample was dosed with the higher $T_{\text{fil}}$ and the pressure at $1.0 \times 10^{-7}$,
the TPD peak area was approximately 1/5 of the earlier trial. The peak position was consistent with the high temperature desorption peak. The results suggest that the energy of the AO, rather than AO flux, is the critical factor controlling the surface structure and subsurface oxygen formation on Ag(111).

In summary, the surface of oxidized Ag(111) depends strongly on the exposure conditions. Under gentler conditions and lower fluxes, surface oxides and subsurface oxygen are formed. Under more vigorous conditions, subsurface oxygen does not appear to form, and instead the surface roughens and bulk-like Ag$_2$O forms on the surface. This has relevance to surface structures of actual catalysts. The availability of O in a surface oxide likely differs from the thin films of bulk oxide. If the catalytic surface is exposed to a high rate of O atoms, Ag$_2$O could be favored, and the necessary subsurface oxygen to activate adsorbed oxygen in the partial oxidation on silver would not be present.
CHAPTER FIVE

SAMPLE TEMPERATURE EFFECTS ON THE ADSORPTION AND ABSORPTION OF OXYGEN ON AG(111)

It is well established that subsurface oxygen forms on Ag(111) after exposure to gas phase atomic oxygen or high pressure O₂ exposures.⁶⁶ What is far less clear is what factors enhance or disfavor the formation of O₅₉, and how the electronic and geometric structure of Ag(111) is altered by O₅₉. Most previous studies have focused on the formation of surface oxides and their structures.⁶⁵ Subsurface oxygen has received far less attention.¹⁶⁷ This project looked at the role of Ag(111) sample temperature in the formation of O₅₉ and surface structures. The findings have direct consequences for the understanding of how the active oxygen species for Ag(111) catalyzed ethylene epoxidation may be formed and how the structure of a silver catalyst will evolve under conditions of high oxygen coverage.

Ag is readily oxidized at atmospheric and elevated pressures, but UHV preparation of oxidized Ag(111) surfaces is challenging. The sticking probability of O₂ on Ag(111) is approximately 1.0 × 10⁻⁶, so comparatively high pressures are required to oxidize Ag(111) with O₂.⁷⁷ To avoid high pressure dosing, alternative oxidants are necessary. NO₂, atomic oxygen,¹⁶⁸ and O₃ can all be used to oxidize Ag. In spite of the carefully controlled conditions, a complex variety of surface structures and oxygen species have been observed or proposed. Oxygen species described by various authors
have included chemisorbed oxygen\textsuperscript{76}, both weakly and strongly bound to the
surface\textsuperscript{161,157}, O\textsubscript{γ}\textsuperscript{166}, nucleophilic and electrophilic oxygen\textsuperscript{169}, bulk oxygen\textsuperscript{67}, and O\textsubscript{sub}.\textsuperscript{170}

The surface structures thus far identified or proposed include $p(4 \times 4)\textsuperscript{82,83}$, $c(3 \times 5\sqrt{3})\textsuperscript{82}$, $p(4 \times 5\sqrt{3})\textsuperscript{81}$, $c(4 \times 8)\textsuperscript{171}$, $p(\sqrt{3} \times 3\sqrt{3})R30°\textsuperscript{166}$, $(7 \times \sqrt{3})\text{rect}\textsuperscript{172}$, and striped\textsuperscript{81,171} structures
as well as $p(7 \times 7)\textsuperscript{17}$, AgO, and Ag\textsubscript{2}O oxide structures. As yet, there is little correlation
between the oxidant, temperature, or flux, and the resultant surface. It seems that many of
the structures are nearly isoenergetic and often have very similar stoichiometry, further
complicating efforts at unravelling the structure and reactivity of oxidized silver surfaces.

A causal link between surface preparation and surface oxide structure remains
undeveloped. It is also not clear how the various surface structures are tied to the active
oxygen species in partial oxidation reactions. Recent progress has suggested that O\textsubscript{sub}
plays a key role in the nature of the O/Ag(111) surface and in partial oxidation
catalysis.\textsuperscript{173-175} However, surface oxygen\textsuperscript{66}, surface defects\textsuperscript{176}, and surface oxides\textsuperscript{155,78}
have also been proposed as factors in the selectivity of Ag catalyzed ethylene
epoxidation.

NO\textsubscript{2} has been used to study the oxidation of many metal single crystals including
Pt(111)\textsuperscript{35}, Pd(111)\textsuperscript{177} and Ru(001).\textsuperscript{178} On Ag(111), NO\textsubscript{2} dissociates into NO and O at
temperatures above 215 K.\textsuperscript{179} Bare et al first used NO\textsubscript{2} to study the oxidation Ag(111).\textsuperscript{34}
They used a microcapillary doser and were not able to quantify the flux NO\textsubscript{2} hitting the
surface, they only reported their results in arbitrary dose units. Based on LEED data, Bare
et al., concluded that NO\textsubscript{2} dosing, which was done at 508 K, led to a well-ordered (4 × 4)
surface. TPD results yielded a $\theta_{O}$ of 0.51 ML. However, the study was done before the
current model of the $p(4 \times 4)$ structure, and the higher coverage was not considered an
issue. A few years later, Huang and White revisited the issue of NO\textsubscript{2} dosing.\textsuperscript{150} They found that above 450 K, only O remained after dosing with NO\textsubscript{2}. Dosing at 508 K resulted in a well-ordered \(p(4 \times 4)\) structure. In 2013, Wintterlin’s group used a different NO\textsubscript{2} dosing method to produce a previously unreported \((7 \times \sqrt{3})\) structure.\textsuperscript{172} They proposed that the new structure was composed of the active O species for ethylene epoxidation. The method they used involved dosing Ag(111) with NO\textsubscript{2} at 500 K, then annealing briefly at 580 K. After the cycle was repeated multiple times, the new O species was observed. While their results do show that NO\textsubscript{2} dosing on Ag(111) can lead to structures other than the \(p(4 \times 4)\) structure, there was no evidence of significant subsurface oxygen accumulation. All of the TPD studies using NO\textsubscript{2} on Ag(111) support the idea that after single doses, O only adsorbs to the surface, and that saturation dosing with NO\textsubscript{2} is a reliable way to calculate monolayer coverage.

For this project, the Ag(111) crystals were cleaned by the same method described in Chapter 4. The AO dosing procedure was also the same as the one used in Chapter 4. NO\textsubscript{2} dosing was done through a leak valve and directed doser. The doser consisted of a tube connected to the leak valve with a 10 \(\mu\)m aperture at the end. To dose, the sample was positioned \(\approx 1\) cm from the aperture and the leak valve was opened. Figure 60 shows an STM image taken after dosing with NO\textsubscript{2} at 500 K. Consistent with previous studies, the predominate structure observed after dosing with NO\textsubscript{2} at 500 K or higher was \(p(4 \times 4)\). However, other structures were sometimes present. Figure 60 shows a column of \(p(4 \times 5\sqrt{3})\) structures near a screw dislocation. Small areas of bare Ag are also visible on either side of the screw dislocation. Figure 61 shows an image also taken after dosing with NO\textsubscript{2} at 500 K. It shows a large defect free \(p(4 \times 4)\) domain.
Figure 60. STM image after dosing with NO$_2$ at 500 K. Most of the surface is covered with well-ordered $p(4 \times 4)$ domains. A column of $p(4 \times 5\sqrt{3})$ structures is visible near a screw dislocation across the middle of the image. $T_s = 20$ K, $I_T = 300$ pA, $V_b = 0.8$ V.

Figure 61. STM image of $p(4 \times 4)$ domain after dosing with NO$_2$ at 500 K. No defects are visible within the $p(4 \times 4)$ domain. $T_s = 20$ K, $I_T = 300$ pA, $V_b = 0.8$ V.
When dosing with NO$_2$ with a sample temperature below 500 K, large $p(4 \times 4)$ domains were still observed. However, $p(4 \times 5\sqrt{3})$ structures also comprised a significant portion of the surface. The $p(4 \times 5\sqrt{3})$ structures were not generally observed in separate domains. They were most often seen as columns extending through the $p(4 \times 4)$ domains.

Figure 62 shows an image of the Ag(111) surface after dosing with NO$_2$ at 490 K. Columns of $p(4 \times 5\sqrt{3})$ structures are visible within the $p(4 \times 4)$ domains. Sets of $p(4 \times 5\sqrt{3})$ columns are aligned along one of three axes, each rotated by 60°. Despite the mixture of the two structures, there is no evidence of single defects or even small islands of defects. All of $p(4 \times 5\sqrt{3})$ structures are connected to other $p(4 \times 5\sqrt{3})$ structures in the columns.

![Figure 62. STM image of $p(4 \times 5\sqrt{3})$ defects after dosing with NO$_2$ at 490 K. The surface is covered by $p(4 \times 4)$ domains with multiple columns of $p(4 \times 5\sqrt{3})$ structures. $T_s = 20$ K, $I_T = 250$ pA, $V_b = 0.9$ V.](image-url)
Figure 63. STM image after dosing with NO$_2$ at 490 K. The surface is covered by a mixture of $p(4 \times 4)$ and $p(4 \times 5\sqrt{3})$ structures. The arrow indicates a previously unreported structure. $T_s = 20$ K, $I_T = 350$ pA, $V_b = 0.8$ V.

Although the $p(4 \times 4)$ and $p(4 \times 5\sqrt{3})$ structures were most common after dosing with NO$_2$, other structures were also present. Figure 63 shows the surface after dosing with NO$_2$ at 490 K. At the top of the image is an area of unreconstructed Ag surrounded by $p(4 \times 5\sqrt{3})$ structures. In the lower portion of the image, there is also a $p(4 \times 4)$ domain. The arrow points to a new unidentified structure. Figures 64 and 65 show an additional structure observed after NO$_2$ dosing. While these structures have not been seen before, they appear to be similar to the structures that are typically observed. This suggests that they are likely a new arrangement of the six and ten Ag atom triangles rather than entirely new formations.
Figure 64. STM image of multiple structures after dosing with NO\textsubscript{2} at 490 K. The upper right portion of the image contains a previously unreported structure $T_s = 20$ K, $I_T = 350$ pA, $V_b = 0.8$ V.

Figure 65. STM image of new structure after dosing with NO\textsubscript{2} at 490 K. $T_s = 20$ K, $I_T = 250$ pA, $V_b = 0.8$ V.
Even though NO\textsubscript{2} dosing does not always yield a uniform structure across the entire Ag(111) surface, it does appear to produce only a single overlayer. The $p(4 \times 4)$ (0.375 ML), $p(4 \times 5\sqrt{3})$ (0.375 ML), $c(3 \times 5\sqrt{3})$ (0.4 ML) structures all have similar coverage\textsuperscript{171}. Because of this, NO\textsubscript{2} was used to calculate saturation coverage for TPD purposes. Figure 66 shows TPD spectra taken after dosing Ag(111) with NO\textsubscript{2} at 500 K. Combined with STM images, the fact that the peak does not grow with longer dosing shows that the surface is saturated and O\textsubscript{sub} is not forming. The integral of this peak was then used to determine the coverages for AO exposures.

Figure 66. TPD spectra after dosing with NO\textsubscript{2} at 500 K. All three doses resulted in almost identical TPD spectra showing that the surface was saturated and O\textsubscript{sub} did not form. Ramp rate = 4 K s\textsuperscript{-1}.

In order to look at the effect of sample temperature, the Ag(111) sample was dosed with AO using the lower T\textsubscript{fil} setting. The temperature of the filament was $\approx$ 1,750 K for all of the experiments. This setting was chosen to avoid the formation of bulk
Ag$_2$O. Figure 67 shows TPD data after exposing the sample to AO for 5 min at 475 K, 490 K, 500 K, 510 K, and 525 K.

Figure 67 shows that there are two distinct temperature regimes when dosing Ag(111) with AO. When the temperature of the sample was ≤ 500 K, two desorption peaks form. Dosing with the sample temperature above 500 K resulted in only a single desorption peak. Taken with the earlier experiments which showed that the formation of a second desorption peak was associated with O$_{\text{sub}}$, Figure 67 suggests that small changes in T$_{\text{sam}}$ have a significant impact on the nature of surface and subsurface O formation. To investigate this effect further, additional experiments were carried out with the sample at 490 K, 500 K, and 525 K.
Figure 68. TPD spectra after AO dosing at 525 K. Dosing at 525 K results in a single desorption peak with a $T_{\text{max}}$ of 580 K. For some trials, the T ramp was extended to 950 K. No significant high temperature desorption peak was observed. The higher baseline of the 10 min dose (green) is most likely due to O accumulation on the sample mount.

Figure 68 shows that dosing with the $T_{\text{sam}}$ at 525 K, yields only a single desorption peak. The size of the peak initially grows linearly with dose length, but by five minutes, the peak saturates. Comparison with the NO$_2$ data shows that the peak saturates at $\approx 0.4$ ML, which is essentially the same as $\theta_0$ for the three well-known surface structures. Even after 10 minutes, the high temperature peak near 800 K that was seen with the higher $T_{\text{fil}}$ was not observed. While no higher temperature peak was present, for dose lengths of 10 minutes or longer, the baseline did not fully drop after the desorption peak. This is most likely the result of desorption from the Cu block holding the sample rather than the sample itself.
Figure 69. LEED pattern after 30 s AO dose at 525 K. Dim spots are visible around the sharp bright spots of the (111) structure. E = 52 eV.

Figure 69 shows a LEED image taken after dosing the sample with AO for 30 s at 525 K. The sharp bright hexagon is consistent with diffraction from the Ag(111) surface. Around each of the bright spots, faint hexagons are also present. The pattern suggests that while other structures are beginning to form, the surface retains a well-ordered and largely (111) structure. STM images taken after short AO doses at 525 K are consistent with this. Figure 70 shows two images after a 30 s AO dose with a T_{sam} of 525 K. The image on the left shows a well-ordered p(4 × 5√3) domain on the upper right side of the image. On the left side of the image is an area of bare Ag that is not resolved. The height profile of the image showed that the boundary between the bare Ag and the p(4 × 5√3) structures was not a step edge. Both areas are on a single terrace which has been partly oxidized. The image on the right shows a p(4 × 5√3) domain which has none of the typical bands of c(3 × 5√3) defects.
Figure 70. STM images after 30 s AO dose at 525 K. The image on the left shows a $p(4 \times 5\sqrt{3})$ domain and an area of bare Ag. $T_s = 20\, \text{K}, I_T = 250\, \text{pA}, V_b = 0.7\, \text{V}$. The image on the right shows a well-ordered $p(4 \times 5\sqrt{3})$ domain. $T_s = 20\, \text{K}, I_T = 350\, \text{pA}, V_b = 0.75\, \text{V}$.

Longer AO doses at 525 K yielded similar results. Less of the surface was bare, but the predominate surface structure remained $p(4 \times 5\sqrt{3})$. Figure 71 shows a LEED diffraction pattern after a 2 min AO dose at 525 K. The bright hexagon due to the Ag(111) surface is still visible, but the spots indicating larger structures are significantly brighter than with the 30 s dose.

Figure 71. LEED pattern after 2 min AO dose at 525 K. Although the spots due to the Ag(111) surface are still present, spots from larger structures more visible. $E = 52\, \text{eV}$. 
Figure 72 shows two images taken after dosing with AO for 2 min at 525 K. The predominate structure is still $p(4 \times 5\sqrt{3})$, but there are significantly more $c(3 \times 5\sqrt{3})$ structures present than with shorter doses. The image on the left shows a terrace covered with $p(4 \times 5\sqrt{3})$ and $c(3 \times 5\sqrt{3})$ structures extending all of the way to the step edge. The image on the right shows an image of another area of the surface after a 2 min dose. The $p(4 \times 5\sqrt{3})$ and $c(3 \times 5\sqrt{3})$ are almost evenly mixed, but there are no isolated instances of either structure.

Five minute or longer AO doses at 525 K led to a completely saturated surface that was otherwise the same as shorter doses. Figure 73 shows a LEED and an STM image taken after a 5 min AO dose at 525 K. The LEED pattern is virtually the same as the pattern after a 2 min dose shown in Figure 71. The STM image on the right is also similar to images taken after shorter AO doses at 525 K. The surface is covered mainly
by $p(4 \times 5\sqrt{3})$ structures. There is only a single band of $c(3 \times 5\sqrt{3})$ structures running through the image.

![LEED and STM images](image)

Figure 73. LEED and STM images after 5 min AO dose at 525 K. Both images are similar to results after shorter doses at 525 K. In the STM image, there is only a single band of $c(3 \times 5\sqrt{3})$ defects running diagonally across the image. $T_s = 20 \text{ K}$, $I_T = 280 \text{ pA}$, $V_b = 1.0 \text{ V}$.

AO dosing with the sample at 500 K produced significantly different results. The TPD results in Figure 75 show that $O_{\text{sub}}$ begins to form by 5 min. However, the 5 and 10 min TPD spectra are virtually the same. Both of the desorption peaks appear to saturate by 5 min when dosing at 500 K. These results seem to contradict earlier data that did not show evidence of saturation when dosing at 500 K. The TPD data in Figure 67 shows that small variations in sample temperature near 500 K have a significant impact on $O_{\text{sub}}$ formation. Sample temperature was monitored by a thermocouple spot welded to the side of the crystal. Between the experiments reported in Chapter 4 and these experiments, the crystal was re-polished. A new Ag(111) crystal was also used for some of these trials to ensure that the results were reproducible. This required different thermocouples to be
welded to the crystals, likely resulting in a shift in the temperature readings by several K. This is supported by a shift in the $T_{\text{max}}$ of approximately 5 K in the TPD spectra of the two sets of experiments. The difference between these results and some of the results in Chapter 4 highlights the importance of small changes in sample temperature.

![Figure 74](image.png)

Figure 74. TPD spectra after AO dosing at 500 K. Dosing at 500 K results in two desorption peaks which both saturate by the 5 min dose.

The TPD data in Figure 74 shows that for doses $\leq 2$ min, the results are nearly identical when dosing at 525 K or 500 K. Short doses at both temperatures result in a single desorption peak with a $T_{\text{max}}$ of 580 K that grows linearly with dose length. LEED and STM results also show sample temperature does not change the nature of the surface for AO doses less than 2 min. Figure 75 shows a LEED pattern and an STM image obtained after dosing with AO for 30 s at 500 K. In the LEED pattern, the bright hexagonal pattern due to Ag(111) is clearly visible. Additional spots indicating larger structures are also visible. All of the spots are sharp, indicating that the surface has a large degree of order. The LEED pattern is similar to the pattern obtained after all doses
at 525 K. The STM image on the right is also very similar to the results from dosing at 525 K. The surface is covered primarily by $p(4 \times 5\sqrt{3})$ domains with very few defects. There are some areas of bare Ag visible, which is consistent with the results from dosing at 525 K.

Figure 75. LEED and STM images after 30 s AO dose at 500 K. The results are nearly identical to results from dosing at 525 K. The LEED pattern shows evidence of Ag(111) and some larger structures. The STM image shows the most common structure is $p(4 \times 5\sqrt{3})$. $T_s = 20$ K, $I_T = 280$ pA, $V_b = 1.0$ V.

For AO doses $\geq 2$ min with a $T_{sam}$ of 500 K, sample temperature begins to affect $O_{sub}$ and surface structure formation. The TPD data in Figure 74 shows that with a sample temperature of 500 K, the surface saturates and $O_{sub}$ begins to form by 5 min. Figure 76 shows a LEED image and an STM image of the surface after a 2 min AO dose at 500 K. The LEED image is very different than the previous LEED images. The spots of the Ag(111) structure are still visible, but the pattern for larger structures has changed. STM images also showed a different surface. Although there was still a mixture of structures, $c(3 \times 5\sqrt{3})$ domains, such as the one shown in Figure 76, were more prevalent than the
$p(4 \times 5\sqrt{3})$ domains seen with shorter doses. The most striking difference was the presence of $c(4 \times 8)$ domains which had not been seen with other doses. Figure 77 shows an STM image of a $c(4 \times 8)$ domain. The $c(4 \times 8)$ structure is significantly different than the other structures and does not contain Ag atom triangles.

Figure 76. LEED and STM images after 2 min AO dose at 500 K. The linear pattern and smaller hexagons visible in previous LEED patterns have been replaced a complex pattern of distinct spots. $T_s = 20$ K, $I_T = 350$ pA, $V_b = 0.75$ mV.

Figure 77. STM image of $c(4 \times 8)$ domain after 2 min AO dose at 500 K. $T_s = 20$ K, $I_T = -340$ pA, $V_b = -400$ mV.
For 5 min doses, the difference between 500 K and 525 K dosing was even more significant. The surface was covered almost entirely by $c(3 \times 5\sqrt{3})$ and $c(4 \times 8)$ domains.

Figure 78 shows a mix of structures around a screw dislocation after a 5 min AO dose. On the left and top of the image are $c(3 \times 5\sqrt{3})$ domains with bands of $p(4 \times 5\sqrt{3})$ structures running through them. The area in the lower right part of the image looks similar to areas of bare Ag after shorter doses. However, it was determined that $c(4 \times 8)$ domains were unresolved when imaged with conditions that were used with all of the other structures observed. Clear resolution of $c(4 \times 8)$ domains was only possible when the bias voltage was reduced or reversed. Figure 79 shows an image of the $c(4 \times 8)$ domain and a model of the structure.

Figure 78. STM image of mixed domains after a 5 min AO dose at 500 K. The unresolved area in the lower right is a $c(4 \times 8)$ domain. $T_s = 20$ K, $I_T = 300$ pA, $V_b = 0.75$ V.
When the surface was dosed with AO at 500 K for longer than 5 minutes, the entire surface was covered with the stripe pattern only previously seen as a small domain by Besenbacher’s group. Figure 80 shows an STM image of the surface after a 10 min dose at 500 K. Thin and thick stripes are intermixed across the terrace. There is a step edge running vertically across the image near the left side. It is noteworthy that the pattern of thick and thin stripes continues across the step edge. This is completely different than the other O/Ag structures where the orientation of domains above and below a step edge are completely independent. The stripe pattern also appears to always extend all the way to both the top and bottom of step edge. Figure 81 shows a closer image of the stripe pattern. While there is clearly a smaller unit cell to the stripes, further resolution of the subunits was not possible. Figure 82 shows a LEED image of the stripe pattern. The LEED shows a well-resolved pattern exhibiting 3-fold symmetry.
Figure 80. STM image of stripe pattern and step edge after 10 min AO dose at 500 K. \(T_s = 20 \text{ K}, I_T = 300 \text{ pA}, V_b = 0.9 \text{ V}\).

Figure 81. STM image of stripe pattern after 10 min AO dose at 500 K. \(T_s = 20 \text{ K}, I_T = 300 \text{ pA}, V_b = 350 \text{ mV}\)
Figure 82. LEED image of stripe pattern after 10 min AO dose at 500 K. The diffraction pattern shows clear 3-fold symmetry. $E = 52$ eV.

AO dosing at 490 K shows different results than dosing at higher temperatures. Figure 83 shows the TPD results after dosing with AO at 490 K. For short doses, the results are similar once again. A single desorption peak with a $T_{\text{max}}$ of 580 K is present for AO doses < 2 min. After only 2 minutes, a lower temperature peak begins to form, initially appearing as a shoulder on the peak at 580 K. Between 2 and 5 minutes, the peak at 580 K only increases slightly. In contrast to dosing at 500 K, the lower temperature peak continues to increase. By 10 minutes, the lower temperature peak completely swamps the higher temperature peak, but the $T_{\text{max}}$ of the two peaks is still $\approx 580$ K. Importantly, because the peak does not appear to saturate, significantly more than 0.4 ML of O$_2$ desorbs. This suggests that at 490 K, substantial amounts of O$_{\text{sub}}$ are forming.
Figure 83. TPD spectra after AO dosing at 490 K. Desorption after short doses is similar to the results for other dosing temperatures. Longer doses result in a lower temperature desorption peak that does not saturate.

Figure 84. STM images after 30 s AO dose at 490 K. $T_s = 20$ K, $I_T = 280$ pA, $V_b = 1.0$ V.
As with dosing at 525 K and 500 K, 30s AO doses at 490 K resulted in a mix of $p(4 \times 5\sqrt{3})$ domains and chemisorbed O on bare Ag. The image on the right in Figure 84 shows a triangle of bare Ag within a $p(4 \times 5\sqrt{3})$ domain. The dark spots within the triangle are most likely chemisorbed O. Similar images were seen by King’s group during the first STM study of the O/Ag system.

Figure 85. LEED pattern after 2 min AO dose at 490 K. $E = 52$ eV.

Figure 85 shows a LEED image of the surface after a 2 min AO dose at 490 K. The pattern has some similarity to the pattern observed after dosing for 2 min at 500 K, but the Ag(111) spots are less distinct and there is more streaking of the other spots. STM images after 2 min dosing at 490 K showed even more substantial differences. The image on the left of Figure 86 shows thin chains stretching across terraces from both sides of a step edge. These chains were found across the Ag surface and were not localized to a particular region of the crystal face. Further resolution of the surface structure shows that the chains are surrounded by $c(4 \times 8)$ domain structures, as seen in the image on the right in Figure 86. From the STM images, it appears that the chains form after the $c(4 \times 8)$
structure has been fully formed since topographic analysis show the chains to be higher relative to the $c(4 \times 8)$ structure.

Figure 86. STM images after 2 min AO dose at 490 K. (L) Chains stretch to both sides of the step edge. $T_s = 20$ K, $I_T = 300$ pA, $V_b = 0.95$ V; (R) $T_s = 20$ K, $I_T = 280$ pA, $V_b = 400$ mV.

Figure 87. STM images showing chains forming on $c(4 \times 8)$ structure. (L) $T_s = 20$ K, $I_T = 250$ pA, $V_b = 600$ mV; (R) $T_s = 20$ K, $I_T = 280$ pA, $V_b = 400$ mV.
Figure 88. LEED pattern after 10 min AO dose at 490 K. Unlike pattern after dosing at 500 K, pattern has 2-fold rather than 3-fold symmetry. E = 52 eV.

Longer AO doses at 490 K yield the same stripe pattern seen after 10 minute doses at 500 K. Figure 88 shows a LEED image taken after a 10 min AO dose at 490 K. The pattern is similar to the one seen after 10 minute dosing at 500 K, but shows only 2-fold symmetry compared to 3-fold symmetry. On the right side of the pattern in the middle there are three spots instead of the line of spots seen after dosing at 500 K. The most probable explanation is that the stripe pattern does have 3 possible orientations, each rotated by 60°, on the (111) surface as would be expected. However, as the image in Figure 80 showed, the orientation of the pattern can continue across step edges. Also, after extended dosing, extremely large domains were observed. The difference in the LEED patterns between the 490 K and 500 K doses is most likely the result of only domains with two of three possible orientations being within the LEED beam at the time the image was recorded. Figure 89 shows that the stripe pattern formed after extended dosing at 490 K is the same as the pattern formed at 500 K.
As detailed above, without the presence of $O_{sub}$, STM imaging after AO dosing always showed a mixture of surface structures or a mixture of surface structures and bare Ag(111). In almost all cases, the structures observed have been previously reported. Some new structures, shown in Figures 63-65, were observed after NO$_2$ dosing. Small areas of several previously unreported structures were also seen under various AO dose lengths and surface temperature conditions. One structure, shown in Figure 90, was seen along $p(4 \times 5\sqrt{3})$ domain boundaries. The hexagonal pattern is similar to a $p(4 \times 4)$ structure, but appears to be comprised of Ag decamers rather Ag hexamers. The second structure, shown in Figure 91, was observed within larger $p(4 \times 5\sqrt{3})$ domains and it also appears to be the result of Ag decamers. The $p(4 \times 5\sqrt{3})$ structure consists of back-to-back Ag decamer pairs separated by two Ag hexamers. In the structure seen in Figure 91, the hexamers separating two columns of decamer pairs appear to be missing. The result is
a four Ag decamer wide column. These double wide columns were observed stretching out from step edges in otherwise defect free $p(4 \times 5\sqrt{3})$ domains.

Figure 90. STM image of hexamers of 10 Ag atom triangles. $T_s = 20$ K, $I_T = 300$ pA, $V_b = 1.1$ V.

Figure 91. STM image of double wide set of Ag decamers. $T_s = 20$ K, $I_T = 300$ pA, $V_b = 0.9$ V.
Across the three sample temperatures of 490 K, 500 K, and 525 K, the largest deviation from TPD trends, LEED patterns, and STM images was seen after longer AO dosing between 525 K and the two lower temperatures. The TPD data showed that with the increase in AO oxygen exposure, at 525 K, the surface saturated, but significant subsurface O did not form. Surface saturation, and no subsurface O formation, resulted in a consistent LEED pattern and only minor variations in STM imaging. A sample temperature of 500 K resulted in a varied TPD spectra for doses longer than 1 min when compared to the saturated 525 K TPD spectra. The larger integrated area, coupled with the evolution of a second desorption peak, showed that subsurface oxygen was formed. As the TPD spectra evolved from the peak seen at 525 K, there was an evolution in the LEED pattern and structures present in STM imaging. When the 500 K TPD data is compared to the data collected at 490 K, there are similarities in the peak evolution. Despite the 490 K TPD spectra having a larger TPD integrated area, the LEED patterns and STM imaging show similar surface structures under the two lower temperature dosing conditions. As with the 500 K dosing, the additional O$_2$ must be due to subsurface O adsorption.

Based on the TPD data, as well as LEED and STM imaging, the temperature of the Ag(111) sample initially has no effect on surface reconstruction. STM images suggest that the AO induced reconstruction of the Ag(111) surface initially favors the $p(4 \times 5\sqrt{3})$ structure. Conversely, with NO$_2$ dosing, the predominate structure is the more stable $p(4 \times 4)$ structure. For all three dosing temperatures, domains of $p(4 \times 5\sqrt{3})$, with some patches of $c(3 \times 5\sqrt{3})$ and $p(4 \times 4)$ are formed after short AO doses. At low coverages, the growth of existing domains is favored on Ag(111) regardless of temperature. At the
studied temperatures, the initial structures formed using AO or NO$_2$ determined which
surface structures predominated until the surface was saturated. It is only after the surface
is saturated that the effect of sample temperature becomes important. When dosing at 525
K, the TPD shows little or no additional O$_2$ accumulation with longer doses and STM
imaging shows that the surface stays essentially the same. When dosing with a sample
temperature $\leq$ 500 K, the TPD data shows subsurface O forms after surface saturation.
Only after O$_2$ coverage exceeds saturation do STM images show significant areas of $c(4 \times 8)$. Longer doses then lead to the formation of chains within the $c(4 \times 8)$ structures and
ultimately to the stripe pattern. This suggests that sample temperature has an important,
but indirect, effect on Ag(111) surface reconstruction. The main factor that sample
temperature controls is subsurface absorption. Subsurface O formation then strongly
influences surface structure formation.
CHAPTER SIX
CONCLUSIONS AND FUTURE RESEARCH

Atomic oxygen is an effective method to produce high coverage oxide structures on Rh(111) and Ag(111). On Rh(111), dissociative adsorption of O$_2$ and the adsorption of atomic oxygen yield similar surface structures dominated by the (2 × 1) adlayer. TPD and AES results showed that the surface was quickly saturated by O$_2$ exposure. However, even after extended O$_2$ dosing, (2 × 2) islands were still present. Higher effective coverages, up to 2.2 ML, were possible when using atomic oxygen. STM images clearly showed that despite high effective oxygen coverages, the surface was not uniformly covered with the (1 × 1) adlayer structure corresponding to $\theta_O = 1.0$ ML. Taken together, these results show that oxygen was readily embedded into the Rh subsurface without first saturating the surface with a (1 × 1) adlayer. These findings show that at all observed coverages multiple adlayer domains coexist, and uptake into the subsurface of the metal depends strongly on the nature of the incident oxygen.

Oxidation of Ag(111) is more complex than Rh(111) and depends strongly on the exposure conditions. Using lower energy atomic oxygen yielded well-ordered surface oxides and, at some temperatures, subsurface oxygen. Under more vigorous conditions, subsurface oxygen does not appear to form, and instead the surface roughens as apparent domains of thin films of bulk-like Ag$_2$O develop on the surface. This has relevance to surface structures of actual catalysts. The availability of O in a surface oxide likely
differs from the thin films of bulk oxide. If the catalytic surface is exposed to a high rate of O atoms, Ag$_2$O could be favored, and the necessary subsurface oxygen to activate adsorbed oxygen in the partial oxidation on silver would not be present.

Based on the TPD data, as well as LEED and STM imaging, the temperature of the Ag(111) sample initially has no effect on surface reconstruction. For all three dosing temperatures, mixed domains of $p(4 \times 5\sqrt{3})$, $c(3 \times 5\sqrt{3})$, and $p(4 \times 4)$ are formed after short AO doses. STM images suggest that the AO induced reconstruction of the Ag(111) surface generally favors the $p(4 \times 5\sqrt{3})$ structure. Conversely, NO$_2$ dosing at the same temperature results in the formation of the more stable $p(4 \times 4)$ structure with some $p(4 \times 5\sqrt{3})$ defects.

At low coverages, the growth of existing domains is favored on Ag(111) regardless of temperature. At the studied temperatures, the initial structures formed using AO or NO$_2$ determined which surface structures predominated until the surface was saturated. It is only after the surface is saturated that the effect of sample temperature becomes important. When dosing at 525 K, the TPD shows little or no additional O$_2$ accumulation with longer doses and STM imaging shows that the surface stays essentially the same. With lower temperature dosing, the TPD data shows subsurface O forms. Only after O$_2$ coverage exceeds saturation do STM images show significant areas of $c(4 \times 8)$. After large $c(4 \times 8)$ domains are present, the formation of chains within the $c(4 \times 8)$ structures begins. Those chains ultimately lead to the stripe pattern. This suggests that sample temperature has an important, but indirect, effect on Ag(111) surface reconstruction. The important factor that sample temperature controls is subsurface absorption. While dosing AO at 525 K only results in the formation of surface
oxide, dosing at 500 K and 490 K results in surface oxide formation as well as subsurface O absorption. The formation of $O_{\text{sub}}$ is critical to the formation of the stripe pattern.

There have been hundreds of papers written on the O/Ag(111) system. Of those, only one previous paper observed the stripe pattern discussed here, and that was only in a small domain.\cite{footnote171} This can be explained by the combination of oxygen source and sample temperature used in these experiments. Dosing conditions which provide enough energy for O atoms to penetrate the surface typically provide the same energy for O atoms to emerge from the subsurface. The method used here is different than the majority of previous experiments because the energy of the incident O atoms in greater than the thermal energy of the Ag(111) crystal. This allows O atoms to penetrate into the subsurface where are thermally equilibrated. Below 500 K, subsurface O can accumulate. The formation of $O_{\text{sub}}$ alters the surface and leads to the stripe pattern. However, the energy of the incident O atoms is also critical. If the energy is sufficiently high, a small amount of $O_{\text{sub}}$ forms, but a bulk-like Ag$_2$O oxide also forms.

Under almost all conditions, with Rh(111) and Ag(111) mix of structures was observed. Variations in the oxygen source, flux, and energy as well as sample temperature did impact the resulting surface and subsurface products. But, while dosing conditions may favor certain products, multiple structures on both Rh(111) and Ag(111) are nearly isoenergetic. This strongly suggests that realistic models of the surfaces under realistic catalytic conditions will need to include coexisting structures. However, under all of the conditions tested, isolated subunits of structures were never observed. The initial formation of any of the structures appears to make additional formation of that
structure more favorable. This suggests that even though high coverage oxidized surfaces may be complex and dynamic, domains of ordered structures are likely to be present.

The work presented in this dissertation has identified conditions which yield a wide variety of surface and subsurface O products on Rh(111) and Ag(111). Additional work is being done these results can be used to develop a better understanding of Rh and Ag catalyzed reactions. XPS studies using the beamline at Argonne National Lab are being done on AO dosed Ag(111) to look at what role the different structures may play in Ag catalyzed ethylene epoxidation. In addition, computational studies are currently being done to determine the structure of the stripe pattern.
REFERENCE LIST


VITA

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