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The Surface Chemistry of Ultrathin Palladium Films on Refractory Metal Single Crystals

by

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B.S., University of Wisconsin - Stevens Point

A thesis submitted to the Faculty of the Graduate School of the University of Colorado in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry and Biochemistry

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The Surface Chemistry of Ultrathin Palladium Films on Refractory Metal Single Crystals
Thesis directed by Associate Professor Bruce E. Koel

The growth and structure of ultrathin Pd films deposited on Mo(100) and the chemisorption properties of ultrathin Pd films on Mo(100) and Ta(110) have been studied. Pd films deposited on Mo(100) at 150 K grow by a layer-by-layer mechanism. Deposition at higher temperatures leads to layer plus crystallite growth.

Chemisorption studies on the Pd monolayer on both Mo(100) and Ta(110) indicate that it has a chemical reactivity similar to Ag. CO is weakly bound to the Pd monolayer on Mo(100) with an adsorption energy of 20 kcal/mole. In contrast, the adsorption energy of CO on bulk Pd(100) is 36.5 kcal/mol. The sticking probability of CO on the Pd monolayer on Mo(100) is also reduced and the propensity for population of atop sites is increased. C2H4 is also weakly bound on the Pd monolayer on Mo(100) and the propensity for reversible adsorption is increased relative to thick Pd films. The adsorption of H2 was studied on the Pd monolayer on both Mo(100) and Ta(110). In both cases a reduced sticking coefficient and a reduction in the hydrogen chemisorption bond strength was observed. A low temperature desorption state attributed to a hydride species was also detected. The amount of H2 desorbing from the hydride state increased with increasing Pd film thickness. NO adsorption on the Pd monolayer on Ta(110) is molecular at 95 K. Heating the surface causes desorption and decomposition of NO and the reaction products N2O and N2 are observed to desorb. A similar reactivity is seen for Ag(111) surfaces. An N2O3 species is also formed for very large NO exposures. Acetylene cyclotrimerization to benzene has been observed to occur on the Pd
monolayer on Ta(110). A flat lying benzene species is formed which desorbs at 400 K. This is the same temperature at which benzene desorption occurs following benzene exposures suggesting that the desorption is not reaction rate limited.

Studies of thicker Pd films show that there is some ability to "tune" the chemistry of the surface by controlling the Pd film thickness. Bulk Pd properties are observed for Pd films greater than five layers thick.
DEDICATION

For Phaedrus

Everyone and no one, a metaphor and a myth.
ACKNOWLEDGEMENTS

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My acknowledgements would not be complete without thanking each and every member of my family. They have all contributed to this work indirectly through their love and support. Special thanks go to my parents who somehow knew not to push during those difficult formative years. See mom, you can screw up and still do OK. Finally, I would like to thank Lisa. Her love and support, limitless patience, and understanding have made all the difference.
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CHAPTER I

INTRODUCTION

Transition metal surfaces readily catalyze many chemical reactions. The activity and selectivity of a metal catalyst is often improved by adding promoters or alloying one metal with a second metal. The enhanced performance which is observed has generally been attributed to geometric (ensemble) effects, electronic (ligand) effects, or a combination of the two. Geometric effects modify the chemistry by changing the availability of active sites on the surface. These include the blocking of sites required for reaction, changes in the surface composition which reduce the active site density, and changes in the active site geometry. Changes in the surface electronic structure can be caused by charge donation or withdrawal or by significant rehybridization of surface atoms. This results in changes in the bonding interactions of reactant and product molecules on the surface.

These effects have been the focus of a great deal of research [1-4], but a detailed microscopic understanding of the important factors which influence heterogeneous catalysis is not yet available. Much of the difficulty arises from the problems associated with determining catalyst composition and structure. This in turn makes it difficult to determine the origin of the changes in the catalyst performance which occur after the addition of promoters or the formation of alloys. Because of the complicated nature of catalysts, studies of the surface chemistry of single crystal surfaces have been undertaken.

The advantage of using a single crystal surface is that the geometric and electronic structure are well defined. Thus, low energy electron diffraction (LEED)
can be used to determine the structure of the clean surface and probe the presence or absence of ordered adsorbate structures. Additionally, many electron spectroscopic techniques can be used to probe the surface chemistry. Auger electron spectroscopy can be used to determine the atomic composition of the surface, photoemission can probe the electronic structure of the surface, and high resolution electron energy loss spectroscopy can be used to gain information about molecular bonding on the surface.

The influence of the surface geometry has been investigated on single crystal surfaces by studying the reactivity of different crystal faces (e.g., (111) versus (110)) [5-8] and by using "inert" site blockers such as Pb and Bi adsorbed on single crystal surfaces [9-11]. The use of inert site blockers allows the determination of ensemble sizes for various chemical processes through statistical modelling [9]. The effects of the electronic structure have been studied using small amounts of promoters such as K or Cs adsorbed on various surfaces [12-14]. The formation and characterization of surface alloys on single crystal surfaces has also been undertaken and holds much promise [15-17].

Another approach to study the effect of electronic structure on surface chemistry, and that used in this thesis, is to deposit a thin metal film on the surface of a dissimilar metal. In the submonolayer regime both geometric and electronic effects will cause changes in the chemistry and these studies are similar to those of surface alloys. However, at the monolayer level the surface will be composed of only one component, the adsorbed metal. Thus, ensemble effects, as traditionally discussed, can be ruled out. Due to interactions with the substrate this adsorbed monolayer will have an altered electronic structure relative to the bulk metal surface of the adsorbate. One can optimistically hope for the ability to form epitaxial overlayers which have an altered electronic structure but retain a constant geometric
structure as the film structure is increased. The objective in these studies is to investigate and compare the chemistry of the ultrathin film (monolayer, bilayer, trilayer etc.) with the chemistry of the bulk single crystal surface of the adsorbed metal with the same symmetry.

Of critical importance to the study of the surface chemistry of thin metal films is the determination of the growth mechanism and structure of the deposited metal. Several review articles which discuss metal-on-metal epitaxy are available [18-21]. Both the submonolayer and multilayer coverage regimes are important.

Depending on the adsorbate-substrate system, adsorbed metal atoms may form two dimensional structures or three dimensional structures in the submonolayer coverage range. A two dimensional phase forms when the bonding of the adsorbed metal is stronger to the substrate than it is to itself. Three dimensional structures form when the opposite is true. The three dimensional structures may be crystallites or liquid droplets depending on the melting temperature of the adsorbed metal. Two dimensional structures may be classified as gases or crystals with the distinguishing characteristic being lateral periodicity for crystals and the lack of lateral periodicity for gases. Two dimensional crystals may be further divided into commensurate and incommensurate phases. Commensurate structures are those in which the periodicity of the adlayer is a simple multiple of the periodicity of the substrate. Incommensurate structures are those in which the periodicity of the adlayer is not a simple multiple of the substrate periodicity. In general there may be a gas phase, several commensurate phases, and several incommensurate phases depending on the adsorbate-substrate system, temperature, and adsorbate coverage.

Above a monolayer coverage the three dimensional (3D) structure must be considered. Three major mechanisms have been identified for an overlayer growing on a substrate [22,23]: (a) the Frank-van der Merwe mechanism (layer-by-layer
growth); (b) the Volmer-Weber mechanism (growth of crystallites without the formation of a complete layer); (c) the Stransi-Krastanov mechanism (formation of one or more complete layers followed by the growth of crystallites). One of the most common ways to distinguish between the different growth modes is to record the Auger electron spectroscopy (AES) signals from the substrate and adsorbate as a function of adsorbate exposure time. Each growth mode produces characteristic Auger signal versus time plots (AST plots) because of the different overlayer film morphologies. These are shown in fig. 1.1 next to an illustration of the respective growth mode. For the Frank-van der Merwe growth mode a linear increase in the adsorbate signal and a linear decrease in the substrate signal is initially observed (fig. 1a and b). This trend continues until the completion of the first adsorbate layer. At this point a change in slope is observed but the adsorbate and substrate signals continue to increase and decrease, respectively, in a linear manner. This leads to a series of straight line segments with abrupt changes in slope at the layer completion points. For the Volmer-Weber growth mode smoothly increasing and decreasing AES signals are observed as a function of deposition time (fig. 1c and d). The adsorbate signal increases and the substrate signal decreases slowly relative to the Frank-van der Merwe growth mode. This is due to the more efficient attenuation of electrons for films grown by a layer-by-layer mode. The Stranski-Krastanov growth mode yields an AST plot which is intermediate between that observed for the Frank-van der Merwe and Volmer-Weber growth modes. This is shown in fig. 1e. For this growth mode the AST plot initially resembles that of a layer-by-layer growth mode but upon formation of crystallites it behaves similar to a Volmer-Weber growth mode.

As briefly mentioned above, metal films adsorbed on the surface of a dissimilar metal are expected to have an altered electronic structure relative to the
Figure 1.1  Comparison of growth modes and the substrate and adsorbate AES signals as a function of adsorbate deposition time.
bulk. There are several factors which are important: (i) lattice strain, (ii) two dimensionality of the film, (iii) bonding interactions between the adsorbate and substrate. Lattice strain may play a role in altering the electronic structure of the adsorbed metal since it will change the lateral interactions between adsorbed metal atoms by changing the interatomic distance from that of the bulk. The two dimensionality of the film may be important simply due to the fact that the thin film will be unable to fully develop the three dimensional band structure of the bulk. Finally, chemical bonding may cause charge transfer or rehybridization of atomic orbitals leading to an altered electronic structure.

Large changes in the electronic structure have been observed for thin films of Pd deposited on refractory metal substrates. For example, photoemission studies of Pd films on Nb(110) and Ta(110) show a reduction in the density of states (DOS) at the Fermi level and a narrowing of the d-band, which is also shifted to higher binding energy [24-28]. This has been attributed to a rehybridization of the d bands at the interface resulting in occupied states with both Pd and Nb character [29]. Additionally, Pd films deposited on refractory metal surfaces have been shown to have altered chemisorption properties relative to bulk Pd surfaces. Many studies have focused on CO adsorption on thin Pd films [30-38]. For example, the Pd-CO bond strength has been measured for the Pd/Nb(110) [34], Pd/Ta(110) [36,38], Pd/W(110) [35,37] and Pd/W(100) [35] systems using TPD and was found to be ≤ 20 kcal/mol in all cases. This can be contrasted with the values of 35 kcal/mol [39] and 36.5 kcal/mol [40] found for the heat of adsorption on the (111) and (100) surfaces of Pd single crystals. UPS studies are consistent with a weakened CO-metal interaction [32,33] for the Nb and Ta systems. While a fair number of experiments have studied CO [30-38], H2 [31,34-36,41-43] and O2 [44,45] on thin
Pd films, essentially nothing is known about the interaction of other molecules on these surfaces.

In this thesis, studies of the growth and stability of Pd films deposited on Mo(100) are discussed in chapter III. This work forms a foundation for the studies of the surface chemistry of Pd films on Mo(100) which are presented in chapter IV-VI. The Mo(100) surface has a larger lattice mismatch with bulk Pd than the bcc (110) surfaces studied thus far [46]. If lattice strain is an important factor in the altered chemistry of Pd thin films, then a larger effect might be expected for Pd/Mo(100). We therefore compare studies of CO, H₂, C₂H₄, and C₂H₂ chemisorption with chemisorption on bulk Pd surfaces and, where possible, previous chemisorption studies on ultrathin Pd films. The surface chemistry of Pd films deposited on Ta(110) is addressed in chapters VII-IX. NO, N₂O, H₂, C₂H₂, and C₆H₆ are investigated. Finally, concluding remarks and suggestions for further work are presented in chapter X.
REFERENCES FOR CHAPTER I


[46] The surface atom density of Pd(111) is $1.53 \times 10^{15}$, for Nb(110) and Ta(110) it is $1.30 \times 10^{15}$, for W(110) and Mo(110) it is $1.42 \times 10^{15}$, for Pd(100) $1.32 \times 10^{15}$, for W(100) it is $1.00 \times 10^{15}$ and for Mo(100) $1.01 \times 10^{15}$. 
CHAPTER II

EXPERIMENTAL INFORMATION

2.1 Apparatus

2.1.1 Ultra-high Vacuum Chamber

In order to study the chemistry and physics of surfaces one must first be able to produce a clean surface. From the molecular theory of gases, the flux of molecules incident on a surface, \( Z \), can be calculated by knowing their molecular weight, temperature, and pressure \([1]\). The relationship between these parameters is given by:

\[
Z = N_A \left( \frac{RT}{2\pi M} \right)^{1/2} = 3.52 \times 10^{22} \frac{P}{(MT)^{1/2}}
\]  

(2.1)

where \( N_A \) is Avogadro's number, \( R \) is the ideal gas constant, \( P \) is the pressure in torr, \( M \) is the molecular weight, and \( T \) is the temperature in Kelvin. For a molecule of mass 28 at 300 K and a pressure of 1 x 10\(^{-6}\) torr, the resulting flux is 3.84 x 10\(^{14}\) molecules cm\(^{-2}\) s\(^{-1}\). If we assume the adsorption probability of the molecule is unity and the surface atom density is 1 x 10\(^{15}\) atoms/cm\(^2\), it is easily seen that the surface will be completely saturated in less than 3 seconds. This severely limits the ability to perform experiments on clean surfaces. It follows that by lowering the pressure to 10\(^{-10}\) torr the time scale for surface cleanliness is increased by four orders of magnitude. This illustrates the need for an ultra-high vacuum (UHV) environment for surface studies.
All of the experiments discussed in this thesis were conducted using the stainless steel UHV chamber shown in figs. 2.1 - 2.3. This chamber has been described previously [2] and has the capability to perform all of the surface science techniques described in section 2.3. A typical base pressure of \(1 \times 10^{-10}\) torr was maintained through the use of a 220 l/s ion pump, a 120 l/s turbo molecular pump, and a titanium sublimation pump. A UHV Instruments Corporation manipulator was used for sample positioning. The manipulator was modified to allow cooling with liquid nitrogen, resistive heating, and electron beam heating. Figure 2.4 is an illustration of the sample mounting block showing the side and top views. A schematic of the electrical circuit used for heating is shown in fig. 2.5. Resistive heating was accomplished by supplying power to the relay (causing the relay to close) and sending electrical current from a 50 A power supply though power feedthroughs to the sample mounting block and the crystal. Electron beam heating was accomplished by biasing the sample with a positive voltage while an electrical current flowed through a small filament mounted behind the sample. The filament was taken from an automobile headlight and the ends of the filament were spotwelded to the two stainless steel post. Tantalum wire (0.1 mm diameter) was wrapped around the ends of the filament and stainless steel posts and spotwelded to the posts to insure a good hold. The distance from the filament to the back face of the crystal was approximately 2 mm. Typically, 4 A of current flowed through the filament with a voltage of 12 V. To heat the crystal, the positive voltage applied to the crystal was slowly increased causing electrons emitted from the filament to be attracted to the crystal. A voltage of 600 V allowed the temperature of the crystal to reach 2700 K. The temperature of the sample was measured by a W-26%Re/W-5%Re thermocouple spotwelded to the side of the sample which was referenced to a second W-26%Re/W-5%Re thermocouple submerged in an ice water bath. The
Figure 2.1 Illustration of two level stainless steel UHV chamber used for all experiments presented in this thesis.
Figure 2.2  Top view of upper analysis level. Instrumentation is available at this level to perform AES, LEED, UPS, and TPD.
Figure 2.3  Top view of lower analysis level. The main feature at this level is the HREELS spectrometer.
Figure 2.4 Illustration of copper mounting block.
Figure 2.5  Schematic of electrical circuit used for resistive and electron beam heating.
voltage reading from the thermocouple was converted to degrees Kelvin by using a polynomial of the form:

\[ T \ (K) = A_0 + A_1 \cdot V + A_2 \cdot V^2 + A_3 \cdot V^3 + A_4 \cdot V^4 \]  

(2.2)

where \( T \) is the temperature in degrees Kelvin, \( V \) is the voltage reading from the thermocouple in millivolts, and \( A_n \) are the polynomial coefficients. Table 2.1 lists the values of the coefficients used for temperatures above and below 273.15 K.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>( T &gt; 273.15 ) K</th>
<th>( T \leq 273.15 ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>273.15</td>
<td>273.15</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>1.285</td>
<td>1.372</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>-0.02309</td>
<td>-0.9408</td>
</tr>
<tr>
<td>( A_3 )</td>
<td>6.658 \times 10^{-4}</td>
<td>-0.7961</td>
</tr>
<tr>
<td>( A_4 )</td>
<td>2.589 \times 10^{-6}</td>
<td>-0.3463</td>
</tr>
</tbody>
</table>

Data acquisition was accomplished with the aid of an IBM-XT computer and a Scientific Solutions interface board. The computer software used was originally written by Mike Bartram in IBM compiled basic with assembly code routines written by Jeff Kingsley. The software was modified by Mark Jones and the author to run in Quick Basic 4.0.

2.1.2 Instrumentation

The top level of the UHV chamber is shown in fig 2.2. At this level the chamber was equipped with a cylindrical mirror analyzer (CMA) which was used for kinetic energy analysis of electrons. Auger electron spectroscopy (AES) was
performed with the use of the on-axis electron gun contained in the CMA. The top level of the chamber was also equipped with a quadrupole mass spectrometer, low energy electron diffraction (LEED) optics, and a sputter ion gun. In addition, a Pd metal doser and two gas dosers are available at this level. The bottom level of the UHV chamber is shown in fig. 2.3. The main feature at this level is the high resolution electron energy loss spectrometer. The analyzer of the spectrometer is moveable to allow off-specular scattering experiments.

2.2 Sample and Reagent Preparation

2.2.1 Single Crystal Preparation

The Mo(100) single crystal (Atomergic Chemical Corp. 99.99%) had a diameter of 10 mm and was 1 mm thick. The initial cleaning procedure included sputtering with 500 eV Ar+ followed by heating to 1100 K in 1x10⁻⁸ torr of O₂ and repeated flashes in vacuum to 2000 K with the use of electron beam heating. The cleanliness of the surface was checked with AES. After the initial cleaning process the main contaminant was oxygen. This was removed prior to each experiment by heating to 2000 K in vacuum. Following this treatment the LEED pattern exhibited sharp spots with the expected symmetry [3].

The Ta(110) crystal was rectangular with dimensions of 6 x 8 x 1 mm. The initial cleaning procedure for this sample involved Ar⁺ sputtering followed by repeated heating to temperatures as high as 2700 K. Typically, twelve to eighteen hours were required to obtain a clean surface after placing the sample in the UHV chamber. Once the initial cleaning was concluded, three to seven flashes to 2500 K were usually sufficient to obtain a clean surface. The clean surface produced a sharp LEED pattern with the expected symmetry [4].
2.2.2 Reagents

Pd was deposited by resistively heating a 0.5 mm diameter tungsten wire which was wrapped with 0.1 mm diameter Pd wire (Alfa 99.997%). The stability of the doser was checked by monitoring the current passed through it with an ammeter. Pd dosing times were controlled by a rotatable metal flag which could stop the flux of Pd atoms from impinging on the surface of interest.

Research purity CO (Matheson, 99.99%) was passed through a liquid nitrogen trap, but was used without any further purification. H₂ (Matheson, PP Grade, 99.9%), C₂H₄ (Scientific Gas Products, 99.9%), C₂D₂ (Cambridge Isotope Laboratories, 99 atom % D), and N₂O (MG Industries, 99.9%) were used as supplied. C₂H₂ (Matheson, 99.6%) was purified using standard glass vacuum line fractional distillation procedures to remove traces of acetone and was stored at pressures less than 1 atmosphere in a glass bulb. NO (Matheson, CP grade) was passed through a dry ice-methanol trap, but was used without any further purification.

All exposures are reported in units of Langmuir (1 L = 1.0 x 10⁻⁶ torr·s). Dosing was accomplished with a microcapillary array (Galileo Electro-optics Inc.) attached to the end of a 1/8 inch stainless steel tube which was "press fitted" into a Varian leak valve. The array collimates the gas flow resulting in an increased flux to the crystal face relative to the expected flux for the same pressure without the array. The flux enhancement factor is dependent on the molecule being dosed and the crystal position. Whenever possible, the flux enhancement factor for the various molecules is reported in the relevant chapters.
2.3 Surface Science Techniques

2.3.1 Auger Electron Spectroscopy (AES)

AES is one of the most important techniques for surface analysis. It can provide qualitative and quantitative information about the elemental composition of the first few layers of a surface [5,6]. Figure 2.6 shows a schematic representation of the Auger process. The first step is the creation of a "hole" in one of the inner shells of an atom by ionization. This ionization can be caused by incident ions, photons, or electrons. Once the core hole is produced, relaxation can occur by filling the hole with an outer shell electron. Filling the core hole may produce sufficient energy to eject a second electron from the atom leaving a doubly ionized final state. This ejected electron is called the Auger electron [7]. The kinetic energy of the Auger electron is given by:

$$E = E_W - E_X - E_Y - U_{eff} \quad (2.2)$$

Incident Particle

Auger electron

\begin{align*}
\text{Step I} & \quad \text{Initial State} \quad \text{Final State} \\
E_W & \quad E_X \quad E_Y
\end{align*}

Figure 2.6 Schematic representation of Auger electron emission.
where $E_w$ is the energy of the initially ionized level, $E_X$ and $E_Y$ are the energies of the outer shell levels, and $U_{eff}$ is a final state interaction term.

Note that $E$ is independent of the energy of the initial ionizing particle. Also, since in many cases $E_w$, $E_X$, and $E_Y$ specify atomic core levels which are specific to each element, the Auger electron has a kinetic energy which is often characteristic of the element from which it is ejected. In general, the incident ionizing particle may cause the ejection of Auger electrons deep within the bulk of a solid. However, electrons originating from deep within a solid can not escape without being inelastically scattered by interactions with the solid. The depth from which an electron can escape from a solid without being inelastically scattered is determined by its mean free path, $\lambda$, which is dependent on its kinetic energy. Most elements can emit Auger electrons in the range of 20 - 1000 eV. Electrons with kinetic energy in this range have small values of $\lambda$. Thus, by monitoring Auger electrons in this energy range AES can be a surface sensitive technique.

A large background of inelastically scattered electrons is created which must be discriminated against when performing the Auger experiment. For all of the work in this thesis this was accomplished by phase sensitive detection of a modulated signal. The first harmonic of the detected electron current from a CMA (a band pass analyzer) provides the first derivative, $N'(E)$, of the AES signal, $N(E)$. Displaying the Auger spectrum as $N'(E)$ versus $E$ suppresses the large background while making the Auger transitions more prominent. Figure 2.7 shows AES spectra displayed in this manner for clean Mo(100), clean Ta(110) and a thick Pd film deposited on Ta(110) and fig. 2.8 shows AES spectra for a Pd monolayer film deposited on Mo(100) and Ta(110).
Figure 2.7 AES spectra of clean Mo(100), clean Ta(110), and a thick Pd film on Ta(110).
Figure 2.8  AES spectra of a one monolayer Pd film on Mo(100) and Ta(110).
2.3.1 High Resolution Electron Energy Loss Spectroscopy (HREELS)

HREELS is a sensitive, non-destructive surface analysis technique that is used to study surface vibrations [6,8,9]. The vibrations may correspond to the vibrations of atoms in the surface layers of a solid or adsorbed molecules. HREELS can be used to determine the molecular structure of an adsorbed species, the molecular orientation, and in some cases the bonding site. Adsorbate coverages as low as 0.1 % of a monolayer may be studied. However, HREELS is not inherently quantitative because the scattering cross-section of a vibrational mode can vary significantly with adsorbate coverage.

In HREELS, a monoenergetic beam of low energy electrons (1 - 10 eV) is focussed onto the sample surface and the scattered electrons are energy analyzed. Loss peaks arise in the acquired spectrum due to the incident electron beam exciting vibrations at the surface and losing a characteristic amount of energy that is equal to the vibrational excitation energy. Two types of electron scattering mechanisms are important for HREELS: dipole and impact scattering. Dipole scattering occurs when the Coulomb field of an incoming electron interacts with the dynamic dipole field of oscillating charges at the surface. This is a long-range interaction and energy exchange takes place far (50 Å) from the surface. This mechanism leads to the dipole selection rule for HREELS: only vibrational modes with a component of the dynamic dipole moment perpendicular to the metal surface will produce energy loss peaks in the specular direction. This selection rule arises because of the screening of a charge on a conducting surface by an image charge induced in the free electrons of the metal. Dynamic dipoles parallel to the surface produce no long range dipole potential while dynamic dipoles perpendicular to the surface produce a long range dipole potential which is enhanced by a factor of two.

Impact scattering occurs when an incoming electron interacts with the ion cores of the adsorbate or substrate. This results in a large momentum transfer and
large scattering angles. The intensity of impact scattering is usually several orders of magnitude weaker than dipole scattering in the specular direction when the incident electron beam energy is low (< 10 eV). The advantage of impact scattering is that by scanning in an off-specular angle, impact scattering losses will be detected while dipole scattering losses will not. This can help determine the geometry of an adsorbate.

2.3.1 Low Energy Electron Diffraction (LEED)

LEED is a technique which provides crystallographic information about the surface and the position of adsorbates relative to the substrate [6,10]. In LEED, a nearly monoenergetic, collimated beam of electrons is focussed on the surface. The electrons are scattered, mainly by the atom cores of the surface, and produce wave interferences that depend strongly on the relative positions of the atoms. The de Broglie wavelength of an electron is given by:

\[ \lambda = \frac{h}{p} = \frac{h}{(2mE)^{1/2}} \equiv \left( \frac{150}{E} \right)^{1/2} \text{Å} \]  

(2.3)

where \( h \) is Plank's constant, \( m \) is the mass of the electron, and \( E \) is the voltage through which the electrons have been accelerated (in volts). A general rule for diffraction phenomena is that the wavelength of the incident particle must be on the order of the size of the aperture or obstacle. Because of this, electrons with kinetic energies between 30 and 300 eV are typically used in LEED experiments. The diffraction pattern formed by the scattered electrons is detected by a fluorescent screen which is in the path of the reflected electrons. The observed pattern is a reciprocal-space representation of the sample surface. Figure 2.9 shows the surface structures and LEED patterns for Mo(100) and Ta(110).
Figure 2.9  Surface structures and LEED patterns for Mo(100) and Ta(110): (a) surface structure for clean Mo(100); (b) LEED pattern for Mo(100); (c) surface structure for clean Ta(110); (d) LEED pattern for Ta(110)
2.3.1 Temperature Programed Desorption (TPD)

TPD is a powerful technique which allows the determination of kinetics and energetics of desorption products and the relative coverages of adsorbed species [6,11,12]. In addition, the technique can be used to determine chemisorption bond strengths, sticking probabilities and the population of different adsorption sites for the same species.

The TPD experiment is performed by adsorbing a gas of interest on a surface while the sample is held at some constant, low temperature. The temperature is then increased while the partial pressures of the desorption products are monitored with a mass spectrometer. The desorption rate can be written as:

\[ \frac{-d\theta}{dt} = v_n \theta^n \exp\left[\frac{-E_d}{RT}\right] \]  

where \( \theta \) is the adsorbate coverage, \( v_n \) is the pre-exponential factor, \( n \) is the desorption order, \( E_d \) is the desorption activation energy, \( R \) is the ideal gas constant, and \( T \) is the temperature. The desorption rate as a function of surface temperature can be analyzed in a number of ways to yield information about \( n \), \( E_d \), and \( v_n \). One of the most simple is Redhead analysis [11]. If the system is rapidly pumped, the temperature is increased linearly with time (\( T = T_0 + \beta t \)), and it is assumed that \( E_d \) and \( v_n \) are independent of surface coverage, the following equations can be written for zero, first, and second-order desorption processes:

\[ \frac{E_d}{R} = \frac{v_0}{\theta_0 \beta} \exp\left[\frac{-E_d}{RT_p}\right] \]  

(2.5)  

(2.5)  

\[ \frac{E_d}{RT_p^2} = \frac{v_1}{\beta^2} \exp\left[\frac{-E_d}{RT_p}\right] \]  

(2.6)  

(2.6)
where $\theta_0$ is the initial surface coverage and $T_p$ is the temperature of the desorption peak maximum. These equations predict different behavior for the desorption peak as a function of the initial surface coverage depending on the desorption order. Simulations of zero, first and second order TPD spectra are presented in fig. 2.10. For zero order, the leading edges of the desorption peaks overlay each other while $T_p$ increases as the initial surface coverage is increased. The desorption rate rapidly falls to zero on the high temperature side of the peak. For first-order, $T_p$ is constant regardless of initial surface coverage and the peak shape is slightly asymmetric. The peak shape for second-order desorption is symmetric about the peak maximum, $T_p$, and $T_p$ shifts to lower values as the initial surface coverage is increased.
Figure 2.10  Computer simulations of TPD spectra calculated for $E_d = 20$ kcal/mol and $\beta = 8$ K/s for zero, first and second order for several initial coverages. The pre-exponentials used are $v_0 = 1.0 \times 10^{28}$ molecule/cm$^2$·s, $v_1 = 1.0 \times 10^{13}$ s$^{-1}$, and $v_2 = 1.0 \times 10^{-2}$ cm$^2$/molecule·s.
REFERENCES FOR CHAPTER II


3.1 Introduction

Much of the structural characterization of Pd films formed on metal substrates has been done on the (110) faces of Nb [1-8], Ta [2,9-11], Mo [12] and W [13-17]. Indications are that Pd grows in a layer-by-layer mode at room temperature on each of these substrates. The first layer initially grows with a structure that is pseudomorphic with the bcc substrate, simply continuing the substrate lattice, but the adlayer undergoes structural changes at Pd coverages of approximately one bcc monolayer, i.e., a Pd coverage equal to the substrate surface atom density. LEED observations of Pd films on Nb(110) and Ta(110) show that a first order structural phase transition takes place within the Pd monolayer. This transition produces linear arrays of extra spots aligned along the shorter axis of the distorted hexagon formed by the bcc (110) surface. For Pd films on W(110) and Mo(110), extra spots in LEED due to a nearly hexagonal, compressed fcc (111) Pd structure are seen during room temperature depositions. As the Pd thickness increases, fcc (111) planes in the Nishiyama-Wassermann orientation, i.e., Pd[110] parallel with the substrate [001], are eventually formed on all four (110) metal surfaces. Annealing experiments on all of these surfaces have shown the pseudomorphic Pd monolayer to be stable to at least 1000 K. Thicker films of Pd agglomerate into three dimensional (3D) crystallites during heating. Clear evidence of alloying is seen for the Pd/Mo(110) system upon annealing, once the Pd films are
thick enough to remain continuous [12]. It was proposed that Mo diffuses into the Pd overlayers to form Pd-Mo alloy islands leaving a thin Pd film at the surface.

Pd adsorption and film growth have also been studied on the W(100) surface [13,18]. In this case, the first three layers grow in a layer-by-layer fashion and are pseudomorphic with the substrate. As a result, these layers are highly strained. Above three bcc monolayers, additional deposited Pd is incorporated into the first three layers. Complex LEED structures were observed for thick Pd films and were attributed to distorted fcc Pd(111) planes. Thermal desorption spectra of Pd from W(100) does not show the usual two peak structure seen for many metal-on-metal systems, i.e., a low temperature state from sublimation of multilayers and a high temperature peak from monolayer desorption, but rather three peaks. This indicates a complex interaction of Pd with the substrate.

In the present work we investigate Pd films deposited on Mo(100). The growth mechanism and thermal stability of the Pd overlayers are characterized by using AES, LEED and TPD of Pd. Specifically, we want to determine the similarities and differences between the two faces of Mo, (100) and (110), and also compare these results on Mo with those on the W(100) and W(110) surfaces.

3.2 Experimental Information

These experiments were carried out in the stainless steel UHV chamber described in chapter II. AES was carried out using a double pass CMA with a coaxial electron gun operating at 3 kV and 20 µA. The electron beam was at normal incidence to the sample and a modulation voltage of 6 V\text{pp} was used. The base pressure of the chamber was 5 x 10^{-11} torr. The heating rate in TPD experiments was 8 K/sec.
3.3 Results

3.3.1 Pd Film Growth

AES was used to determine the Pd film growth mode and to calibrate the Pd coverage. AES measurements were conducted by monitoring the Mo 186 eV and the Pd 330 eV derivative Auger signals as a function of Pd dosing time, t. All AES spectra were recorded with a peak-to-peak modulation voltage of 6 V in order to avoid complications involved in the change in peak shape of the Pd 330 eV transition with Pd coverage [10,12,19]. Several AES spectra obtained in this manner were subsequently integrated to insure that no change in the Pd Auger peak shape was observed as the Pd coverage increased. The AES signals of Pd and Mo, normalized to their respective bulk signals, are shown in figs. 3.1 and 3.2 for three substrate temperatures. Any changes in the Pd dosing rate for measurements at different temperatures were accounted for by immediately remeasuring the growth curve at 150 K after each experiment and correcting the time axis appropriately. In all cases the Mo 186 eV signal remained slightly greater than zero for thick Pd films due to a small overlapping Pd transition. Other Mo transitions were monitored and were found to decrease to zero as the Pd film thickness increased. The data obtained at 450 and 600 K overlay the data for 150 K up to t = 215 seconds. At longer times for the 450 K and 600 K deposition, the Pd signal increases and the Mo signal decreases at a much slower rate relative to the data at 150 K. Between 200 ≤ t ≤ 560 sec, the 450 and 600 K curves continue to overlay each other, but at t = 560 seconds of dosing time the data obtained at 600 K shows a slower growth of the Pd signal and slower decrease of the Mo signal relative to the data taken at 450 K.

Figures 3.3 and 3.4 are an expanded view of the first 800 seconds of the Pd growth curves and clearly show the divergence of the 150 K and higher temperature
Figure 3.1  Pd 330 eV AES signal intensity as a function of Pd deposition time on Mo(100) at 150, 450, and 600 K. Also shown is a model curve for the Pd signal for layer-by-layer growth using Eq. 1 and the following parameters: $\lambda_{pd} = 7.2$ Å, $d = 2.25$ Å.
Figure 3.2  Mo 186 eV AES signal intensity as a function of Pd deposition time on Mo(100) at 150, 450, and 600 K. Also shown is a model curve for the Mo signal intensity for layer-by-layer growth using Eq. 2 and the following parameters: $\lambda_{Mo} = 5.8 \, \text{Å}$, $d = 2.25 \, \text{Å}$. The Mo signal intensity does not reach zero due to an overlapping Pd transition.
Figure 3.3  Pd 330 eV AES signal intensity for the initial stages of Pd deposition. A curve for layer-by-layer growth was fit to the 150 K deposition. The curves shown at 450 K and 600 K are simply drawn to guide the eye.
Mo 186 eV AES signal intensity for the initial stages of Pd deposition. Curves for layer-by-layer growth were fit to the 150 K deposition. The thick solid line represents the fit which includes the clean Mo signal intensity while the dashed line is the fit which omits this point. The curve shown for the 450 and 600 K data is drawn simply to guide the eye.
data at early deposition time. These changes are evidence that significant structural differences exist between the Pd films deposited at 150 K and the Pd films deposited at 450 and 600 K above \( t = 200 \) sec. Differences also exist between the film deposited at 450 K and the film deposited at 600 K above \( t = 560 \) sec. This behavior has been seen in many metal-on-metal systems [20] and is typically attributed to the adsorbed metal forming 3D crystallites, thus reducing the rise of the overlayer signal relative to that seen for two dimensional (2D) growth. The 3D character in a film can vary with temperature, since different crystallite shapes and sizes can be stable on the surface at different temperatures, resulting in further changes in the AES signals as the temperature is increased. This explanation is consistent with the observed AES measurements and indicates that the 3D character of the Pd film increases (crystallites become larger) as the deposition temperature increases.

Two models were used to fit the data in order to elucidate the characteristics of these films. The first model is the ideal layer-by-layer growth mechanism, also known as the Frank-van der Merwe (FM) growth mechanism [21-23]. This type of growth can be described by each Pd 2D layer being formed completely before the subsequent layer begins to grow. In addition the adlayers are pseudomorphic with the substrate and therefore have the same density. In this case, the adsorbate and substrate AES signals at the layer endpoints are given by [21]

\[
\frac{I_A(n)}{I_{A\text{ bulk}}} = 1 - \exp\left(-\frac{nd}{\lambda_A \cos \theta}\right) \quad (3.1)
\]

and

\[
\frac{I_S(n)}{I_{S\text{ bulk}}} = \exp\left(-\frac{nd}{\lambda_S \cos \theta}\right) \quad (3.2)
\]
where $I_A$ is the adsorbate signal, $I_S$ is the substrate signal, $n$ is the number of layers, $I_A^{\text{bulk}}$ is the bulk adsorbate signal, $I_S^{\text{bulk}}$ is the clean substrate signal, $d$ is the layer thickness, $\lambda_A$ is the mean free path (MFP) of the electrons giving the adsorbate signal, $\lambda_S$ is the MFP of the electrons giving the substrate signal and $\theta$ is the analyzer collection angle. In our experiment $\theta = 42^\circ$. A fit of this model to the 150 K data is shown in figs. 3.1-3.4. A good fit was obtained by using $d = 2.25 \, \text{Å}$, $\lambda_{\text{Mo}} = 5.4 \, \text{Å}$, $\lambda_{\text{Pd}} = 7.2 \, \text{Å}$, and a monolayer deposition time, $t_1$, of 225 seconds. The value of $\lambda_{\text{Pd}}$ used compares favorably with that of 7.6 Å calculated from the data of Prigge et al. [18] for Pd on W(100).

In fig. 3.4 we show the Mo AES signal for the first 800 seconds of Pd deposition time and the layer-by-layer fit at 150 K (thick solid line). From this expanded view it is seen that the Mo AES signals at 150 and 450 K initially have a very rapid drop in intensity while the Mo AES signal at 600 K does not. This behavior has also been seen for Pd deposition on Ta(110) and Au(111) substrates in our laboratory, but its physical origin is not understood. Because of this we have also fit the 150 K data omitting the data point corresponding to clean Mo. This is shown by the dashed line in fig. 3.4. In fitting the 150 K data in this way $\lambda_{\text{Mo}}$ was increased to 5.9 Å. None of the other parameters, including $t_1$, needed to be changed. Thus, despite this initial rapid drop, the monolayer completion time, $t_1$, remains at 225 seconds. This rapid initial drop is not critical to the growth determination. Accounting for the initial drop in the Mo intensity results in a better fit for the 150 K data in the initial growth region while a nearly identical fit is obtained at higher deposition times.

Upon further examination, it can be seen that the experimental data for the Pd and Mo AES signals do not follow the model FM curve near the layer completion points, but instead increase and decrease, respectively, more smoothly than
expected. This makes it difficult to identify the monolayer completion time. This is shown clearly for Pd in fig. 3.3 and for Mo in fig. 3.4. One possible explanation is that the growth mode changes as the film becomes thicker. In order to analyze this possibility, we have fit the model to the data taken at 150 K with emphasis on the initial growth (t < 300 seconds) and compared this fit with that obtained by fitting of the entire Pd deposition curve to t = 4000 sec. Figure 3.5 shows that the FM fit to the initial portion of the uptake is good only up to t = 340 sec. Above this time, the experimental data lie above the predicted curve. Since the layer-by-layer growth mode is the most efficient mechanism for increasing the adsorbate AES signal, this could only occur if the second and subsequent layers grew with a higher density than the first monolayer, i.e., more Pd is incorporated into the layers. The driving force for this occurrence is to relieve the large lattice strain which would be present in the first two pseudomorphic layers of Pd. The interatomic distances of Pd(100) and Mo(100) are 2.75 Å and 3.15 Å, respectively. This results in a 12.7% strain in both the (001) and (010) directions and causes a reduction in the surface atom density of 23.6% relative to Pd(100). Incorporation of additional Pd into the layers exceeding the pseudomorphic monolayer has previously been used to explain the deviation of the experimental data from the expected FM growth in the case of Pd on W(100) [18] in which a similar lattice mismatch occurs.

In order to estimate uncertainties in our coverage and structure determination we have also modeled the experimental data at 150 K with a 3D crystallite (Volmer-Weber, VW) growth mechanism. In the crystallite model we use here, discussed in detail by van Delft et al. [24], Pd grows as three dimensional rectangular crystallites and the base of these crystallites is allowed to expand as the Pd coverage increases. The adsorbate and substrate AES signals are given by:
Figure 3.5  Comparison of the Pd 330 eV AES signal intensity for Pd growth on Mo(100) at 150 K to layer-by-layer model curves. The thick line is a fit to data for the entire film while the thin line is a fit with emphasis on the first 300 seconds. The arrows indicate where each fit predicts the monolayer completion point.
\[
\frac{I_A}{I_{bulk}} = \rho \{1-(1-a)^j\} + (1-a)^j a \theta_{j+1}
\]

and
\[
\frac{I_S}{I_{bulk}} = 1 - \rho + \rho s^j - s^j(1-s) \theta_{j+1}
\]

Here \(\rho\) is the relative coverage of the crystallite foot, \(a\) is the monolayer adsorbate Auger signal, \(s\) is the substrate monolayer transmission, \(j\) is the number of layers formed (these layers do not necessarily cover the entire surface) and \(\theta_{j+1}\) is the relative coverage of the layer which is forming. If it is assumed that the coverage, \(\theta\), is proportional to time (\(\theta = ct\)) and that the growth rate of the crystallite foot is proportional to the free uncovered substrate surface, then \(\rho\) is given by:

\[
\rho = 1 - \exp(-vct).
\]

The parameter \(v\) is then a measure of lateral growth relative to the total crystallite growth. When \(v = \infty\), an ideal FM growth is obtained. The growth is through local condensation for \(1 < v < \infty\) and for \(v \leq 1\), the growth is via 3D crystallites. In addition to \(v\), the values of the adsorbate Auger signal at one monolayer, \(a\), the monolayer transmission for the substrate, \(s\), and the monolayer deposition time are varied to obtain the best fit. The monolayer adsorbate Auger signal, \(a\), is related to the adsorbate MFP, \(\lambda_A\), through equation (1):

\[
a = \frac{I_A(1)}{I_{bulk}} = 1 - \exp\left[\frac{-d}{\lambda_A \cos \theta}\right]
\]

where \(I_A(1)\) is the Auger signal for one monolayer of adsorbate. Similarly the substrate monolayer transmission, \(s\), is determined by the substrate MFP, \(\lambda_s\), through equation (2):

\[
s = \frac{I_S(1)}{I_{bulk}} = \exp\left[\frac{-d}{\lambda_s \cos \theta}\right]
\]
where $I_S(1)$ is the Auger signal for the substrate with one monolayer of adsorbate on it. Thus, the values of $a$ and $s$ depend on $\lambda_A$ and $\lambda_S$. For the Pd transition at 330 eV, $\lambda_{PD}$ values from 5.8 Å [17] to 8.16 Å [12] have been reported. As a starting point, 7.2 Å was used which is the value determined by the best fit to the FM growth. The other parameters were then varied to obtain the best fit for the 3D crystallite growth mode. The result is shown in fig. 3.6 by the thin solid line which clearly fits the data quite well. The resulting parameters are $\lambda_{MO} = 5.47$ Å, $v=1.1$ and a monolayer deposition time of 215 seconds. According to this model, the Pd begins growing two dimensionally but each successive layer starts to form before the previous layer is completed. This type of growth has been described as a simultaneous multilayer growth [21] or local condensation. Due to the low adatom mobility the impinging Pd atoms stick at their point of impact. This freezes in a non-equilibrium structure in the Pd film. It is known from UHV microscopy studies [25] that the number density of clusters increases with decreasing temperature as smaller nuclei become stable on the surface. Thus, the clusters are reduced to single atoms in the low temperature limit. It is this type of distribution which will result in similar AES plots as the FM growth mode and cause the "rounding" at the expected break points in the AES growth curves as has been shown previously [26,27]. Modeling the data in this way points out that even if the AES growth curve is initially linear, a small amount of crystallite growth may be present. It must be emphasized that this is not a unique fit and that fits of equal quality were obtained for different values of $\lambda$, monolayer deposition times and values of $v$. Even if a unique fit could be obtained it is difficult to use this model in a quantitative manner due to the potentially unrealistic crystallite shape and lack of knowledge about the distribution of crystallite shapes and sizes. It is likely that the disagreement of $t_1$ in our data is somewhat less than shown in fig. 3.6 since the cluster growth model
Figure 3.6 Comparison of the Pd 330 eV AES signal intensity for Pd growth on Mo(100) at 150 K to layer-by-layer growth and crystallite growth curves. The thick line is from the layer-by-layer growth model and the thin line is from the crystallite growth model.
overestimates the 3D character of the films due to the imposition of a rectangular crystallite shape and therefore predicts a monolayer completion time which is too short. Rather, it is more likely that the crystallites are pyramidal or hemispherical [24].

As mentioned above, we are particularly interested in the calibration of the monolayer deposition time, $t_1$, at 150 K. In order to estimate the uncertainty associated with this determination we have taken into account the range of monolayer deposition times predicted by all the fits to the data. Using these values (including the VW growth) an uncertainty of ±20% results. This amount of uncertainty is, no doubt, common to many studies of metal-on-metal systems, but an estimate of the error limits in the film coverage has only rarely been reported.

From all of the simulations, it is clear that there is only a small deviation from the ideal layer-by-layer growth at 150 K. The fit of the layer-by-layer model curve to the initial stage of growth suggests that deviation from ideal layer-by-layer growth begins in the second layer when the film becomes more dense. The high quality fit of the layer-by-layer model to the entire deposition curve and the crystallite growth fit imply the deviation from ideal layer-by-layer growth is present throughout the uptake but is quite small. Because of the low temperature it is unlikely that a Pd atom would be able to surmount the barrier associated with incorporation into an existing layer. Because of this we favor local condensation which mimics layer-by-layer growth as the best description of the growth at 150 K although, we can not entirely rule out the growth of one pseudomorphic layer followed by the growth of more dense layers. We therefore base our assignment of $t_1 = 225$ on the best fit of the entire growth curve to the ideal FM growth, keeping in mind that there will be some small amount of defects in the film and an associated uncertainty of ±20% in the coverage determination.
LEED observations after Pd film deposition at 150 K showed the (1x1) pattern of the substrate and an increase in the background intensity. The (1x1) pattern persisted for films as thick as 20 layers. No additional spots were observed at any coverages in the as deposited films. Since the LEED studies show a pattern consistent with pseudomorphic growth, we define the Pd monolayer to be a bcc (100) layer with a surface atom density equal to the Mo(100) substrate, and subsequently refer to the Pd coverage, $\theta_{\text{Pd}}$, referenced to $\theta_{\text{Pd}} = 1$ at this density.

Modeling of the 450 and 600 K data was also attempted with the ideal FM and the crystallite growth modes discussed above. Neither of these models fit the data with good agreement over the entire range. Because of this, two models of layer-plus-cluster growth (Stranski-Krastanov, SK) were then used in order to estimate the average 3D cluster thickness of the films deposited at 450 and 600 K. We first used an idealized model of layer plus island growth that grows clusters of a fixed depth which are restricted to grow laterally until a uniform film is obtained. This corresponds to drawing a straight line between the monolayer end point and the layer of appropriate thickness. This model has recently been used by Taylor et al. [27] to estimate the 3D character of Ag on Cu(110). Using this procedure, we find that clusters four layers thick model the 450 and 600 K data in the initial cluster regime very well, but deviates from the data for $t > 500$ sec. We then used an SK growth model which allows the cluster base to expand as the adsorbate coverage increases, as explained above for the VW growth mode. We find that this model, with initial growth of a 2D layer followed by clusters four layers thick, fit the 450 K data well up to $t = 900$ sec and the 600 K data up to $t = 560$ sec. For $560 \leq t \leq 1600$ sec the data obtained at 600 K could be modeled well with crystallites 14 layers thick. These results are shown in fig. 3.7. By modeling the 450 and 600 K data in this way it is clear that the structure of the Pd film does not remain constant as it
Figure 3.7  Comparison of the Pd 330 eV AES signal intensity for Pd growth on Mo(100) at 450 and 600 K with layer-by-layer and layer-plus-cluster growth models.
grows thicker, but instead the size and shape of the clusters changes as a function of the Pd coverage. Again a unique fit can not be obtained due to a lack of knowledge of the crystallite size and shape. It is important to point out that a similar behavior of the AES signals is expected for alloy formation between the adsorbate and substrate. While it seems unlikely for alloying to occur at these relatively low temperatures, we can not rule out this possibility especially in light of the low temperature alloying seen in the Pd/Mo(110) system [12].

3.3.2 Thermal Stability of Pd Films

Annealing experiments were carried out on films of various thicknesses in order to characterize their thermal stability. Figure 3.8 shows a plot of the Pd Auger signal versus annealing temperature. The Mo AES signal of all the films studied showed complementary stability and change. This is shown in fig. 3.9. The $\theta_{\text{Pd}} = 0.5$ and $\theta_{\text{Pd}} = 1.2$ films are stable up to a temperature of 1325 and 1200 K, respectively, as measured by AES. For $\theta_{\text{Pd}} = 0.5$, annealing temperatures exceeding 1325 K cause a sharp drop in $\theta_{\text{Pd}}$ to occur due to desorption and/or interdiffusion of Pd and Mo. A similar behavior is seen for the $\theta_{\text{Pd}} = 1.2$ film at temperatures exceeding 1200 K. The Pd signal reaches zero by 1450 K in both cases. For $\theta_{\text{Pd}} = 2.2$, a slow decrease in the Pd signal begins at approximately 400 K and continues until 870 K. At this point a rapid drop occurs, followed by another slow decrease to 1250 K. Interdiffusion and/or desorption of Pd then causes the Pd signal to rapidly decrease to zero by 1450 K. The thick ($\theta_{\text{Pd}} > 20$) Pd film shows very similar behavior to the $\theta_{\text{Pd}} = 2.2$ film, but with decreases in the Pd signal at slightly higher temperatures. This is probably due to our inability to see small changes in these thick films.

The observed changes in the Auger signals of both Pd and Mo indicate important structural changes occur in the thicker films upon heating above 150 K.
Figure 3.8 Pd 330 eV AES signal intensity as a function of annealing temperature for several Pd film thicknesses.
Figure 3.9 Mo 186 eV AES signal intensity as a function of annealing temperature for several Pd film thicknesses.
There appears to be four annealing stages. The first stage extends up to 400 K. In this region the Pd layers are fairly stable. In the second stage, from 400 to 870 K, Pd films exceeding $\theta_{\text{Pd}} = 1$ begin to form 3D clusters. In the third stage, which extends from about 870 to 1200 K, Pd films exceeding $\theta_{\text{Pd}} = 1$ either form larger 3D clusters or begin to alloy with the substrate causing a rapid drop in the Pd AES signal at 870 K. This could be the onset of alloying and the formation of a relatively stable alloy could account for the stability to 1200 K. Above 1200 K, desorption and interdiffusion become fast and a drastic reduction in the Pd AES signal is observed.

The annealing behavior of Pd films was also investigated with LEED. At temperatures below 300 K, it has been reported that clean Mo(100) reconstructs to give a quartet of spots around the (1/2, 1/2) positions with a splitting of 1/8 to 1/9 that of the normal spots [28]. This was not observed during our LEED experiments possibly due to a small hydrogen, carbon, or oxygen contaminant which is known to impede the reconstruction [28], although AES gave no indication of their presence. Other investigators have also not seen this pattern. Deposition of $\theta_{\text{Pd}} = 0.5$ at 150 K caused a small increase in the background intensity, but no new spots. Upon annealing to 600 K, a fuzzy c(2x2) pattern was observed. This pattern has also been reported for Ag and Cu on Mo(100) [29] and could be due to randomly distributed c(2x2) islands since the coverage is near 0.5 monolayers. This pattern persists up to 1300 K. Deposition of $\theta_{\text{Pd}} = 1$ at 150 K produced an increased background intensity with no additional spots. New spots were not observed until the film was annealed to 1300 K. This produced a c(6x2) pattern. For a $\theta_{\text{Pd}} = 2$ film, no new LEED spots were observed until it was annealed to 1500 K. This produced a faint c(2x2) structure. Annealing to this temperature causes Pd to desorb and AES showed that only 0.5 monolayers of Pd was left on the surface. Thus, this
pattern is most likely due to randomly distributed c(2x2) islands. For thick Pd films ($\theta_{\text{Pd}} \equiv 20$) a complex LEED pattern was seen at 450 K. When the film was annealed to 900 K, this pattern evolved into a $(2\sqrt{2} \times \sqrt{2}) R45^\circ$ pattern. This structure has also been observed for thick Pd films on W(100) [18] and was attributed to distorted Pd(111) planes, although this did not account for all of the observed spots. Annealing between 900 and 1300 K resulted in complex LEED patterns which could not be interpreted by us in a meaningful way without additional studies. At 1300 K the 1x1 pattern of the substrate returned and the AES signals corresponded to those of $\theta_{\text{Pd}} = 1.5$. However, at these high temperatures alloying almost certainly occurs and this can be interpreted simply as the pseudomorphic Pd monolayer on top of an alloy structure.

Desorption of Pd from Mo(100) for various films is shown in fig. 3.10. Only one desorption peak is seen for temperatures up to 1530 K, the highest temperature that we studied. The spectra for $\theta_{\text{Pd}} \geq 3.6$ somewhat resemble that expected for zero order desorption kinetics. However, a small amount of "undercutting" in the initial stages of desorption and the high temperature tails of the peaks which do not suddenly fall to the baseline indicates more complex kinetics than simple zero order. Arrhenius plots yield an activation energy of desorption, $E_d = 100 \pm 4$ kcal/mole for these curves. This value is higher than the bulk sublimation energy of Pd which is 93 kcal/mole [30] and indicates that Pd desorption is influenced by the substrate even for thick films. For $1.4 \leq \theta_{\text{Pd}} \leq 3.6$ monolayers the desorption spectra are symmetric about the peak maximum, more resembling first or second order kinetics, but the temperature of the peak maximum increases with increasing Pd coverage. No Pd desorption was detected for $\theta_{\text{Pd}} \leq 1.1$ due to either a poor signal-to-noise level for this amount of Pd or no Pd desorption at these coverages. For all Pd coverages studied, AES spectra taken after TPD show 0.1 to
Figure 3.10 Pd TPD spectra for several initial Pd coverages on Mo(100)
0.2 monolayers of Pd remaining in the surface region. One possible explanation of the unusual desorption curves is that Pd desorption is occurring from a Pd-Mo alloy. For $\theta_{\text{Pd}} \leq 1$, the Pd diffuses into the bulk of the crystal. For thicker films, alloy formation occurs at low temperatures, at 800 K or even lower. As the temperature is increased above 1250 K, Pd at the surface begins to desorb and Pd in the near surface region diffuses to the surface and this is the rate limiting step for Pd desorption. First order kinetics of diffusion results in the desorption peak being symmetric about the peak maximum. Pd is more readily available at the surface as the films become progressively thicker and the peaks take on a nearly zero order peak shape.

3.4 Discussion

In the Pd/Mo(100) system at 150 K, two dimensional Pd layers are formed with layer disorder and/or non-ideal layering. This non-ideal layering causes "rounding" observed in the AES measurements of the Pd deposition. From the AES data we can not uniquely determine the extent to which clustering occurs or the distribution of shapes and sizes of the clusters. However, based on the results of the fit with the crystallite growth mechanism and good overall agreement with the layer-by-layer fit it can be inferred that the growth is mostly two dimensional with only a small amount of defects in the film due to the limited adatom mobility. LEED observations of the "as-deposited" film show only an increased background intensity which is consistent with this description of Pd growth.

The growth mechanism clearly changes as the temperature of deposition is increased. This can be attributed to a change from a two dimensional layer-by-layer (FM) growth to a two dimensional layer plus 3D island (SK) growth. By 450 K the Pd adatoms become more mobile and are able to agglomerate into 3D crystallites. These clusters are on average four layers thick in the initial cluster regime. The
difference between the films deposited at 450 and 600 K could be a change in the sizes and shapes of crystallites. This is shown by modeling with the SK growth mode, but we can not rule out the possibility of alloy formation or a combination of these effects. Studies of the Pd/Mo(110) system concluded that alloy formation begins at 750 K [12]. Since the (100) face of Mo is more open than the (110) face, Pd on Mo(100) may be susceptible to alloying at even lower temperatures.

Annealing experiments are also consistent with this description of Pd film growth. Films of $\theta_{Pd} \leq 1$ are stable to high temperature. This is likely due to a strong Pd-Mo bonding interaction. Thicker films undergo structural changes upon annealing indicative of metastable layers. These layers form large 3D crystallites upon heating which results in the decrease of the Pd and increase of the Mo AES signals. It is clear from TPD experiments that a Pd-Mo alloy is formed at some point. Unfortunately, TPD only gives information about the system being studied at the desorption temperature. Because of this we can not determine the exact temperature at which the alloy begins to form.

Comparisons with Pd films on Mo(110) [12] show interesting similarities and differences. A Pd-Mo alloy is formed in the Pd/Mo(110) system and is also seen in this work. This alloy may be composed of Pd-Mo alloy layers with a Pd monolayer remaining on the surface as proposed by Park et al. [12]. Several layers of Pd must be present on the surface for alloy formation to occur at low temperature. No place exchange to form a two dimensional surface alloy occurs for $\theta_{Pd} \leq 1$ up to temperatures where bulk diffusion is expected to occur. This is consistent with surface free energy considerations since the Mo surface free energy of 2.28 J/m$^2$ [31] is much higher than the Pd surface free energy of 1.63 J/m$^2$ [31]. Another similarity is the change in growth mode as the deposition temperature is increased. The transition from 2D growth to layer-plus-cluster growth occurs at 550 K for
Pd/Mo(110) and by 450 K for Pd/Mo(100). LEED observations on both surfaces show that the first layer is pseudomorphic with the substrate lattice. However, above $\theta_{\text{Pd}} = 1$ extra spots appear on the (110) surface which are attributed to a Pd fcc(111) structure. No similar Pd(111) spots were ever observed for Pd/Mo(100) surface and LEED spots characteristic of the substrate spots were visible even for thick films ($\theta_{\text{Pd}} \geq 20$). Thus, it appears that the Mo(100) surface imposes its structure on the Pd layer to a greater degree than the (110) surface. Thick Pd layers are metastable and agglomerate into clusters upon annealing. The first two Pd layers on Mo(110) are stable to nearly 1100 K whereas only the first Pd layer is stable on the (100) face.

Pd layers have been found to grow in a layer-by-layer fashion at room temperature for up to four layers on W(110) [17] and up to three layers on W(100) [18]. On W(100), deviation from the ideal FM growth for Pd coverages greater than three layers was attributed to incorporation of additionally deposited Pd into the first three layers, i.e., an increase in the density of the film. The deviation from layer-by-layer growth which we see for Pd/Mo(100) could likewise be attributed to this effect. However, due to the low adatom mobility at 150 K we feel it is due to imperfect layering. A direct comparison between these two systems is complicated by the difference in temperature of deposition. The Pd/W(100) system was not modeled with a VW growth model in order to determine if imperfect layering could be ruled out. LEED observations of Pd coverages greater than 2.5 monolayers on W(100) show a pattern which, although it does not account for all the spots, has been attributed to distorted Pd(111) planes. This LEED pattern is seen on Mo(100) only after annealing a thick film to 900 K. Alloying will be occurring in the Pd-Mo system so the interpretation of a similar pattern for Pd/Mo(100) is not clear. Annealing experiments of Pd on W(100) show that Pd layers subsequent to the
second one agglomerate into three-dimensional islands while on W(110) only the first layer is stable. This is the reverse of the situation on Mo and is surprising in light of the similar lattice constants and electronic structure of Mo and W. Desorption of Pd from W(110) yields a two peak structure, with the low temperature peak being assigned to desorption of Pd from Pd multilayers and the high temperature peak being due to desorption from the first monolayer on W. More complex Pd TPD spectra are observed on W(100). This complexity in Pd desorption is lacking for Pd on Mo(100).

3.5 Summary

The growth mechanism, structure and thermal stability of monolayer and ultrathin Pd films formed by vapor deposition on Mo(100) were studied. Pd film growth at 150 K is described well by a Frank-van der Merwe (FM) or layer-by-layer growth mechanism with a small amount of layer disorder and/or non-ideal layering. The Pd monolayer is pseudomorphic with the Mo(100) substrate lattice as shown by LEED. Pd films deposited on Mo(100) at 450 and 600 K grow by forming three dimensional (3D) islands on top of an initially formed Pd monolayer, i.e., a Stranski-Krastanov growth mode. Alloying could also explain the AES curves at these temperatures. Thermal desorption of Pd from multilayer films begins at 1250 K with an activation energy of 100 kcal/mol. This is 7 kcal/mol higher than the bulk sublimation energy of palladium due to interaction with the molybdenum substrate and was observed for films as thick as 20 layers. Pd desorption is kinetically limited by decomposition of a Pd-Mo alloy and/or diffusion of Pd from the subsurface layers of Mo to the surface. Annealing studies show that the Pd monolayer is stable to 1200 K, but that agglomeration of Pd into 3D islands and possibly alloy formation occurs upon heating thicker films above 400 K.
REFERENCES FOR CHAPTER III


[22] M. P. Seah Surf. Sci. 32 (1972) 703


CHAPTER IV

CHEMISORPTION OF CO ON ULTRATHIN FILMS OF Pd ON Mo(100)

4.1 Introduction

Discovering the origin of the altered properties of ultrathin Pd films on early transition metals is an important goal for designing surfaces with specific chemical and physical properties. Several proposals can be put forth to explain the observed effects including lattice strain and direct, local bonding interactions. On all of the refractory metal substrates studied thus far, a large lattice mismatch exists between the substrate and bulk Pd. This could reduce the Pd-Pd interactions in the thin Pd films, rehybridizing the Pd and causing the Pd to be more "atomic-like", and thus perturb the bonding of CO to Pd. Another explanation is that charge transfer [1] or rehybridization [2] of Pd occurs as a result of the Pd-substrate interaction.

Previous chemisorption measurements on Pd films formed on the (110) face of bcc substrates have been compared to the Pd(111) surface, but we feel that it is more appropriate to compare our experiments on Pd/Mo(100) with the Pd(100) surface due to structural considerations. We briefly review below some pertinent aspects of CO adsorption on bulk Pd(100). This is by no means intended to be a comprehensive review, but is intended to aid the reader in comparing our results on Pd thin films with those obtained on Pd single crystals.

Park and Madden [3] were among the first to study CO adsorption on the (100) face of Pd. Using LEED, these authors proposed that one CO molecule adsorbs to every two Pd atoms in an alternating bridge-bonded arrangement forming a (2x4)R45° pattern at 300 K. This was followed by papers by Tracy and Palmberg
who extended the LEED observations to higher coverages to reveal a compression structure and who determined the binding energy of CO at zero coverage to be 36.5 kcal/mol. Bradshaw and Hoffmann [6] used IR reflection-absorption spectroscopy and followed the CO stretching frequency, $v_{CO}$, as a function of CO coverage. Initially $v_{CO}$ occurs at 1895 cm$^{-1}$, but continuously shifts to higher frequencies at higher $\theta_{CO}$, reaching 1949 cm$^{-1}$ at $\theta_{CO} = 0.5$ for CO exposure at 300 K. In agreement with LEED studies, this was attributed to CO adsorbed in 2-fold bridge sites. A further shift to higher frequency was found during the compression stage (the commensurate-incommensurate transition) so that $v_{CO} = 1983$ cm$^{-1}$ for $\theta_{CO} = 0.6$. If the compression stage was reached by exposing the surface to $1 \times 10^{-7}$ torr of CO at 300 K, a second band appeared at 2096 cm$^{-1}$. This second band disappeared upon heating to 400 K and re-cooling to 300 K in $1 \times 10^{-7}$ torr of CO or pumping the CO away and was assigned to atop-bonded CO. They postulated [6] that some CO molecules initially adsorb in energetically unfavorable atop sites due to the "fast compression" and reduced mobility at high $\theta_{CO}$. Ortega et al. [7] in IR investigations of CO adsorption at 80 K, found a similar behavior of the C-O stretching frequency although $v_{CO}$ was 1997 cm$^{-1}$ at $\theta_{CO} = 0.81$ at this temperature. They proposed a model in which all of the CO molecules are equivalent in the compression stage (although only a small fraction of the CO molecules can sit in crystallographically distinct bridge sites) and the large shift in $v_{CO}$ is due to both static lateral interactions and vibrational coupling. No atop CO was observed in their study. Behm and co-workers [8] have carried out similar experiments using HREELS. Their results are in general agreement with those of Bradshaw and Hofmann [6] with the exception of a lower initial CO stretching frequency of 1774 cm$^{-1}$. It was proposed that this was possibly due to CO in a highly coordinated site, i.e., a four-fold hollow. TPD of CO adsorbed at
125 K on the Pd(100) surface results in a three peak structure with maxima at 258, 378 and 515 K [9] with an initial adsorption energy between 36.5 [4] and 38.5 kcal/mol [10]. The adsorption energy is constant up to $\theta_{CO} = 0.45$ [10], but decreases rapidly above this coverage possibly due to repulsive interactions between the CO molecules.

In this chapter CO chemisorption studies on ultrathin Pd films on a Mo(100) single crystal substrate are discussed. The Mo(100) surface has a larger lattice mismatch with bulk Pd than the bcc (110) surfaces studied thus far [11]. If lattice strain is an important factor in the altered chemistry of Pd thin films, then a larger effect might be expected for Pd/Mo(100). We will show that Pd films on Mo(100) do have altered CO chemisorption properties relative to bulk Pd(100) and that the size of the effects are comparable to those seen on W(110) [12,13] and W(100) [12], but are not as dramatic as Pd films on Nb(110) [14] and Ta(110) [15,16]. Thus, lattice strain is not sufficient to explain our results and some direct interaction between the Pd adlayers and the substrate is implicated.

4.2 Experimental Information

The apparatus used is described in chapter II. The base pressure of the chamber was $5 \times 10^{-11}$ torr. The heating rate used during TPD experiments was 6 K/sec. All Pd coverages are referenced to the clean Mo(100) surface, with $\theta_{Pd} = 1$ corresponding to a Pd coverage equal to the Mo(100) surface atom density, as described in chapter III. CO exposures were carried out with the aid of a glass capillary array doser with a flux enhancement factor of 20. All CO adsorption experiments were performed on Pd films which had been annealed to 450 K in order to avoid as much as possible any changes in the Pd film structure during subsequent annealing of CO adlayers or TPD experiments.
4.3 Results

4.3.1 CO Chemisorption on a Monolayer Pd Film, $\theta_{pd} = 1$

A CO TPD spectrum after a 0.1 L CO exposure on a pseudomorphic Pd monolayer film at 150 K is shown in figure 4.1. This exposure resulted in a TPD area which was 13% of the TPD area for saturation exposures. If we arbitrarily define the CO saturation coverage as $\theta_{CO} = 1$, then the 0.1 L exposure produces a coverage of $\theta_{CO} = 0.13$. The main desorption peak for this CO coverage is observed at 329 K, with much smaller desorption features seen at 920 and 1018 K. The smaller peaks occur at temperatures where CO desorption from clean Mo is observed by us and others [17] and we attribute them to desorption from the back and edges of the Mo crystal [18]. Thus, only one desorption state is observed at $\theta_{CO} = 0.13$ on the Pd monolayer and it is approximately 175 K below that observed on bulk Pd(100) [7,9,10] for a similar $\theta_{CO}$. A TPD spectrum after a saturation exposure (48 L) of CO on a one monolayer Pd film at 150 K is also shown in fig. 4.1. There is a single, low temperature peak at 319 K due to CO desorption from the pseudomorphic Pd monolayer and a high temperature peak due to desorption from the back and edges of the Mo(100) crystal. Comparison to the 0.1 L CO exposure TPD experiment shows a slightly lower peak maximum for saturation CO exposure and a broadening of the desorption peak towards lower temperatures. This is characteristic of a decreased energy of desorption as $\theta_{CO}$ is increased due to lateral interactions and population of more weakly bound sites.

Figure 4.1 can be contrasted with CO desorption from Pd(100) after saturation CO exposures, which results in a three peak structure with peak maxima at 258, 378 and 515 K [9]. Using Redhead analysis [19], the activation energy for CO desorption from the $\theta_{pd} = 1$ film is found to be approximately 20 kcal/mol.
Figure 4.1 CO TPD spectra from a one monolayer Pd film on Mo(100). The 0.1 L and 48 L CO exposures give $\theta_{\text{CO}} = 0.13$ and 1.0 respectively.
assuming first order kinetics and a preexponential factor of $10^{13}$ s$^{-1}$. This is the adsorption energy since CO adsorption proceeds with only a small (if any) activation energy. Comparison with the CO adsorption energy on the (100) surface of bulk Pd, where $E_{\text{ads}} = 36.5$ kcal/mol [4,5], shows a 45% reduction in the CO-Pd chemisorption bond strength on the Pd monolayer.

HREELS experiments were conducted as a function of CO coverage in order to determine the sequence of population of adsorption sites for CO on the Pd monolayer. This is shown in figure 4.2 for a Pd thickness of $\theta_{\text{Pd}} = 1.0$. Small CO exposures (0.1 L) on this film at 150 K lead to peaks at 310, 1745, 1920 and a small shoulder at 1850 cm$^{-1}$. The peak at 310 cm$^{-1}$ is attributed to the Pd-CO stretching mode, $v_{\text{Pd-CO}}$, and the peaks at higher frequencies are assigned to CO stretching modes, $v_{\text{CO}}$, for CO adsorbed in various sites. The peak observed at 1745 cm$^{-1}$ is due to CO adsorbed on Pd four-fold hollow sites. Occupation of the hollow site is expected to shift $v_{\text{CO}}$ to a lower vibrational energy relative to CO adsorbed in the two-fold bridge sites and has been proposed by Behm et al. [8] to explain their HREELS peak at 1774 cm$^{-1}$. The peak at 1920 cm$^{-1}$ is due to a two-fold bridging CO species as has been previously observed on Pd(100) [6-9]. Additional intensity near 1850 cm$^{-1}$ shows that there is a range of bonding environments for CO at these low coverages. As the CO exposure is increased to 0.6 L, the $v_{\text{CO}}$ peak due to the hollow site disappears and the peaks for the bridging species merge into one peak and shift up in energy to 1995 cm$^{-1}$. This shift to higher energies with increasing $\theta_{\text{CO}}$ has been attributed to vibrational coupling and static lateral interactions [7]. An atop site with $v_{\text{CO}} = 2110$ cm$^{-1}$ is also populated at this CO coverage. This is surprising since population of an atop site would not be expected under these conditions for Pd(100) single crystals even at saturation CO coverages [7]. CO
Figure 4.2 HREELS spectra of CO adsorbed on a one monolayer Pd film for increasing CO exposures. CO Exposures = 0.1 L, 0.6 L, 3 L and 48 L.
exposures up to 48 L on the $\theta_{Pd} = 1.0$ film produce no further changes in the vibrational spectrum.

The population of a more weakly bonded atop site is reflected by the low temperature broadening in the TPD spectra of figure 4.1. HREELS spectra were taken at various temperatures to address this point. Figure 4.3 shows a vibrational spectrum for a saturation CO exposure on a $\theta_{Pd} = 1.1$ film for CO dosed at 150 K and a vibrational spectrum acquired after heating to 450 K. At 150 K, both two-fold bridge and atop sites are populated for saturation CO coverages on the Pd monolayer. Heating to 450 K removes CO bonded at the atop sites and shifts $v_{CO}$ for CO in the bridge site down to 1910 cm$^{-1}$. The hollow site at 1790 cm$^{-1}$ is also seen after the warmup to 450 K. All of the CO desorbs above this temperature.

We can conclude from the uptake and warmup HREELS experiments that the hollow and bridging sites have a higher binding energy than atop sites, which leads to these sites being populated at low coverages (produced either by small exposure or by heating) on the Pd monolayer. Weakly bound atop sites are populated for CO exposures $\geq 0.6$ L.

4.3.2 CO Chemisorption on Pd Films of Increasing Thickness

While the Pd monolayer is quite well-characterized, films thicker than this are more complex in that a small amount of 3D clustering occurs and therefore, a small distribution of Pd thicknesses will be present. This in turn may complicate the interpretation of the chemistry which occurs on these films. However, the chemistry must be investigated to determine if Pd films thicker than $\theta_{Pd} = 1$ have interesting chemisorption properties (and therefore deserve better characterization efforts) and, in fact, the determination of CO adsorption sites may give insight into the Pd film structure.
Figure 4.3  HREELS spectra for a saturation coverage of CO at 150 on the Pd monolayer and after heating to 450 K.
CO TPD spectra after 0.1 L exposures of CO on Pd films at 150 K are shown in fig. 4.4 as a function of Pd film thickness. As the Pd coverage increases, the Pd film thickness increases and the CO desorption state at 329 K for the one monolayer Pd film gradually shifts to higher temperature. The maximum CO desorption temperature is not yet reached for $\theta_{Pd} = 7$. For thick Pd films, $\theta_{Pd} \geq 20$, CO desorption with a peak at 499 K is in good agreement with previously reported CO desorption from bulk Pd(100) [7,9,20].

CO TPD spectra after saturation exposures of CO on Pd/Mo(100) at 150 K are shown in figure 4.5 for several Pd coverages. CO desorption is characterized by a peak at 319 K for the one monolayer Pd film. As the Pd coverage increases to $\theta_{Pd} = 2.2$, the centroid of the peak shifts to 375 K and a shoulder appears at 261 K. This shoulder evolves into a peak at 235 K on the $\theta_{Pd} = 5$ film and another new state also appears at 462 K. At this point the desorption spectra look very similar to desorption from bulk Pd(100), albeit with slightly shifted peak maxima. At Pd coverages $\geq 17$ ML CO desorption is again in good agreement with previously reported CO desorption from Pd(100) [9].

We can quantify the CO coverages obtained in the uptake of CO on the Pd films by using the CO TPD area in the experiments shown in Figs. 4.4 and 4.5. For small CO exposures (0.1 L) on the Pd monolayer, a reduction in the amount of CO adsorbed is observed when compared to equivalent CO exposures on thick Pd films. Figure 4.6a shows the CO TPD area as a function of Pd film thickness for constant CO exposures of 0.1 L. This CO dose produces only 66% of the CO coverage on the monolayer Pd film as the thickest Pd film studied ($> 20$ ML). A much smaller (only 10%) reduction in the saturation coverage is seen for saturation CO exposures on the Pd films, as would be expected, and also indicates the number of adsorption sites is nearly independent of film thickness, i.e., no large change occurs in the
Figure 4.4  CO TPD spectra for 0.1 L CO exposures on several Pd films.
Figure 4.5 CO TPD spectra for saturation exposures (48 L) of CO on several Pd films.
Plots used for determining adsorption properties of ultrathin Pd films. (a) CO TPD areas for small (0.1 L) CO exposures from Fig. 4.4 can be used to measure the relative sticking probability of CO on different Pd films. (b) CO TPD areas for saturation exposures (48 L) of CO from Fig. 4.5 can be used to determine the relative amount of CO that can adsorbed on the Pd films.
geometric surface area of the sample due to gross changes in Pd film morphology and roughness. This data is presented in figure 4.6b. This indicates the small TPD area observed for the ultrathin Pd films in Fig 4.6a is not due mainly to a decrease in the number of sites available for adsorption. So, we can infer that a significant drop occurs in the sticking probability of CO on ultrathin Pd films even at 150 K, with the largest effect observed on the monolayer Pd film.

HREELS experiments were also carried out for two CO exposures as a function of Pd coverage on Mo(100). Figure 4.7 shows these results for small CO exposures (0.1 L). The Pd monolayer shows CO stretching modes at 1745, 1925, and a small shoulder at 1850 cm\(^{-1}\) as discussed above. The \(v_{\text{CO}}\) mode at 1745 cm\(^{-1}\) disappears by \(\theta_{\text{Pd}} = 3.1\). Since the CO sticking probability increases slightly as the Pd film thickness increases, the disappearance of the four-fold hollow site mode may be due to an increase in the CO coverage (A similar behavior is seen on Pd(100) single crystals with increasing CO coverage [8]). Two closely spaced \(v_{\text{CO}}\) modes are observed at 1890 and 1925 cm\(^{-1}\) on the \(\theta_{\text{Pd}} = 3.1\) film. These peaks are due to two-fold bridge-bonded CO species. The two modes merge into a single peak at 1950 cm\(^{-1}\) on the \(\theta_{\text{Pd}} \geq 20\) film. No atop species are seen on any of the Pd films at small CO coverages.

HREELS experiments shown in Fig. 4.8 for saturation doses (48 L) of CO on Pd/Mo(100) at 150 K as a function of \(\theta_{\text{Pd}}\) show both bridge-bonded and atop CO on Pd films up to \(\theta_{\text{Pd}} = 5\). On the thick (\(\theta_{\text{Pd}} \geq 20\)) film, \(v_{\text{CO}}\) appears at 2010 cm\(^{-1}\) with a small shoulder at 2100 cm\(^{-1}\). This is attributed to CO adsorbed in two-fold bridging sites with a very small amount of CO in atop sites. The overlap of these two peaks can account for the slightly higher frequency observed for the two-fold bridging species in our work (2010 cm\(^{-1}\)) compared to that observed by Ortega et al. [7] (1997 cm\(^{-1}\)). While TPD results show nearly bulk behavior for a Pd film
Figure 4.7  HREELS spectra for 0.1 L CO exposures for several Pd films.
Figure 4.8  HREELS spectra for saturation exposures (48 L) of CO for several Pd films.
thickness of 5 layers, HREELS experiments reveal that at this thickness there is still some perturbation in the population in CO adsorption sites compared to bulk Pd(100).

4.3.3 LEED

LEED observations as a function of CO exposure on various Pd films on Mo(100) were conducted at 150 K. Exposure to CO caused an increased background intensity. The background intensity increased with CO coverage and no new ordered patterns due to CO were ever observed. This is consistent with the absence of the formation of an ordered CO overlayer at low temperature on Pd(100) [7].

4.3.4 Consideration of the Activation Energy of Desorption of CO

In section 3.1.1 we discussed a rough determination of the activation energy for desorption, $E_a$, of CO from a Pd monolayer film. Using Redhead analysis [19] and assuming a pre-exponential factor of $10^{13}$ s$^{-1}$ and first order desorption kinetics we arrived at $E_a = 20$ kcal/mol. A useful check of the accuracy of the results obtained from Redhead analysis, or for that matter any procedure which attempts to get energetic and kinetic information from TPD data, is to calculate or simulate a spectrum from the derived parameters and compare it to the experimental data. Figure 4.9a shows the results of this comparison for CO desorption following a small (0.1 L) CO exposure from a $\theta_{Pd} = 1$ film using the values from Redhead analysis. While the temperature of the peak maximum and the leading edge of the simulated spectrum agree well with the experimental data, the overall shape of the spectra are quite different, with the simulated spectrum being approximately twice as high and half as wide as the experimental peak. Figures 4.9b - d show similar comparisons for thicker Pd films. For these Pd films, while the temperature of the
Figure 4.9  Comparison of experimental CO TPD spectra from several Pd films with simulated TPD spectra. The thick solid lines represent the experimental data. The dashed lines correspond to simulated TPD spectra using values of $E_a$ which were derived from Redhead analysis while the thin solid lines correspond to simulated TPD spectra using values of $E_a$ and $v$ derived from plots of $y$ vs. $1/T$. (a) $\theta_{Pd} = 1$, (b) $\theta_{Pd} = 2.3$, (c) $\theta_{Pd} = 3.8$, (d) $\theta_{Pd} \geq 20$. 


peak maximum of the simulated spectra from Redhead analysis and experimental data agree, the agreement at low temperature gets progressively worse as the Pd film thickness increases. Overall, the simulated spectra are all much narrower than the corresponding experimental TPD spectrum similar to the observations for the $\theta_{Pd} = 1$ film. These comparisons show that while the activation energy derived from Redhead analysis may be approximately correct, a satisfactory fit to the entire TPD spectrum requires more complicated kinetics than simple first order desorption with constant activation energy.

As a second means of analyzing the TPD data, plots of $[\ln(-d\theta/dt) - n*\ln(\theta)]$ vs $1/T$ were constructed for several of the TPD spectra of Fig. 4.4. A parameter, $\gamma$, defined as:

$$\gamma = \ln(-d\theta/dt) - n*\ln(\theta_{CO})$$

(4.1)

is convenient to use in this discussion [21,22]. The desorption rate of CO is $-d\theta/dt$, $n$ is the kinetic order of desorption, $\theta_{CO}$ is the CO coverage, and $T$ is the temperature. Plots of this type yield a straight line for the entire desorption peak with a slope of $-E_a/R$ and an intercept of $\ln(v/\beta)$ ($R$ is the ideal gas constant and $\beta$ is the heating rate) when $n$ is chosen correctly and simple desorption kinetics ($E_a$, $v$, and $n$ are not functions of $\theta$) are observed [21]. Fig. 4.10a shows the results of this treatment for the experimental TPD spectrum shown in fig. 4.9a using $n = 1$. At low temperatures there is an initial linear segment which begins to "roll over" near the TPD peak maximum. The curve then goes through a small minimum and increases again as the last CO molecules desorb. While this analysis does not yield a straight line for the entire desorption spectrum, fitting a straight line to the initial linear segment yields $E_a = 23.5$ kcal/mol and $v = 3.2 \times 10^{15}$ s$^{-1}$. The simulated spectrum which results from using these parameters is shown by the thin solid line.
Figure 4.10 Plots of $1/T$ vs. several $\theta$ for several Pd films. (a) $\theta_{\text{Pd}} = 1$, (b) $\theta_{\text{Pd}} = 2.3$, (c) $\theta_{\text{Pd}} = 3.8$, (d) $\theta_{\text{Pd}} \geq 20$. 
in fig. 4.9a. It can be seen that this treatment does not result in a significantly better fit than that obtained using $E_a$ derived from Redhead analysis, but a slightly higher value of $E_a$ is obtained.

Plots of $\gamma$ vs $1/T$ for thicker Pd films are shown in fig. 4.10b - d. These curves also show an initial linear segment, but show a change in slope in the temperature range of 360 - 400 K. Fitting a straight line to the initial linear segment of these plots results in values of $E_a < 23$ kcal/mol and values of $v < 1.8 \times 10^{10}$ s$^{-1}$ for CO desorption from the thicker Pd films. Using these values of $E_a$ and $v$ in the calculation of simulated spectra gives the results shown by thin solid lines in figs. 4.9b - d. While these simulated spectra very nicely fit the leading edge (low temperature portion) of the experimental data, they give a lower temperature for the peak maxima and are much too narrow compared to the experimental data. If we include all points up to the peak maximum instead of fitting the initial linear segment of the $\gamma$ vs. $1/T$ plots the resulting simulated spectra (not shown) predict the temperature of the peak maximum much better, but are still more narrow than the experimental data and in particular do not match the trailing edge (high temperature).

The failure of these methods to accurately simulate the experimental TPD data implies that desorption of CO from these thin Pd films is more complex than simple first order kinetics. This could possibly be due to coverage dependent kinetic parameters, or very likely, structural changes in the Pd film which occur during the TPD experiment. Small changes in the Pd film morphology such as three dimensional cluster formation could easily alter the bonding site and/or strength and affect the shape of the TPD spectrum. In either case, $E_a$ and/or $v$ would be expected to change as a function of $\theta_{CO}$ and/or temperature. If we assume that $v$ is constant and $E_a$ is a function of coverage, the desorption rate equation [23] can be written as:
Rate = $-\frac{d\theta}{dt} = \frac{v}{\beta} \theta^n \exp\left[\frac{-E_a(\theta)}{RT}\right]$ \hspace{1cm} (4.2)

Taking the logarithm and rearranging yields

$$E_a(\theta) = -RT \left[ \gamma - \ln \left( \frac{v}{\beta} \right) \right]$$ \hspace{1cm} (4.3)

which can be used to extract a value of $E_a$ for each point in a TPD spectrum as a function of coverage [22]. Figure 4.11a shows the coverage dependence of $E_a$ using this method for the CO desorption spectrum shown in 9a using the value of $v$ derived from fig. 4.10a. This shows that at the highest temperatures, very low $\theta_{CO}$, $E_a$ is close to the value seen on bulk Pd(100) [4,10] but rapidly drops off and approaches 23 kcal/mol by $\theta_{CO} = 0.13$. Using this coverage dependence of $E_a$ results in the simulated TPD spectrum (thin solid line) shown in fig. 4.11b. The quality of the fit of the simulated spectrum to the experimental data (thick solid line) is very good compared to the previous treatments. The leading edge of the desorption peak, temperature of the peak maximum and width of the simulated peak are now all very close to that of the experimental data. Spectra simulated with a coverage dependant $E_a$ for the thicker Pd films also showed good fits to the experimental data. Since it is rather unphysical for $E_a$ to simply have such a strong dependence on small CO coverages, we suggest that CO can induce changes in the Pd film morphology at temperatures above 350 K. The simulations show that these effects are smallest on the monolayer Pd film and increase with Pd film thickness. Additionally, $v$ and even $n$ could also change as a function of $\theta_{CO}$ and/or Pd film morphology and obviously further complicates the analysis. Clearly, more careful studies (e.g., equilibrium measurements) of the desorption kinetics are required to determine the cause of the complex TPD spectra we observe.
Figure 4.11  (a) Plot of $E_a$ as a function of CO coverage for a $\theta_{pd} = 1$ film. (b) Comparison of the experimentally observed CO TPD spectrum (thick solid line) and the simulated TPD spectrum (thin solid line) using the coverage dependence of $E_a$ shown in fig. 4.11a.
4.4 Discussion

Our results obtained by using TPD and HREELS clearly show that ultrathin Pd films on the Mo(100) surface have strongly altered CO chemisorption properties when compared to bulk Pd surfaces. The Pd monolayer shows the largest effects, weakly adsorbing CO with an adsorption energy of about 20 kcal/mol. This is a 45% reduction in the adsorption energy when compared to Pd(100). In addition to this decrease, a large drop (34%) in the sticking probability is observed for CO on the Pd monolayer compared to thick Pd films on Mo(100). This is clearly not mainly due to a decrease in the number of binding sites for the Pd monolayer film, since $\theta_{\text{CO}}^{\text{sat}}$ is nearly constant, but rather it is a manifestation of differences in the CO adsorption energy and adsorption kinetics.

Initially CO adsorbs in four-fold hollow and two-fold bridging sites on the Pd monolayer. Atop sites are populated for higher $\theta_{\text{CO}}$. This is the same site preference seen for bulk Pd(100), although atop sites can only be populated on bulk Pd(100) at 300 K if the compression stage is reached rapidly by exposure to 10^{-7} torr of CO [6]. The maximum intensity ratio of atop to bridge-bonded CO on Pd(100) [6] was reported to be 1:3 and was difficult to reproduce. This was attributed to the difficulty of accurately controlling the rate at which the compression stage was reached. An interesting question is whether or not the population of the atop site on our ultrathin Pd films could possibly be due to defect sites, steps, or clusters in the films. Based on the nearly equal HREELS intensities of the atop and two-fold bridge sites, we feel that this is an unlikely explanation. Our previous work is inconsistent with an extremely rough surface especially for the monolayer film. We propose that the population of atop sites is due to the destabilization of CO adsorption in the two-fold bridging sites as a result of weakened back-bonding between Pd and CO. This creates a situation in which CO bonding to atop sites is
only slightly less energetically favorable allowing atop sites to compete with two-fold bridge sites for CO molecules at high CO coverages.

Thicker films of Pd also show altered chemisorption properties. Due to difficulties in preparing "flat" films (some clustering occurs at 450 K) and characterizing these films, \( \theta_{\text{Pd}} \) probably represents some average thickness only. Nonetheless, the influence of Mo(100) on Pd chemistry probably extends through several Pd layers. The Pd-CO bond energy gradually increases as the Pd coverage increases and the films approach bulk Pd properties for \( \theta_{\text{Pd}} > 7 \). We are able to tune the Pd-CO bond energy between 20 and 36.5 kcal/mol by controlling the Pd coverage. The CO sticking probability and the CO adsorption site preference also gradually approach bulk Pd(100) characteristics as the Pd coverage increases and these can be tuned as well.

Comparison of our results to those from Pd films on Mo(110) would be valuable. One study of CO adsorption on Pd/Mo(110) has been carried out previously [24]. Their focus was on Pd films approximately six layers thick and they characterized CO thermal desorption behavior before and after ion bombardment. Because of the different preparation procedures and goals of that work from our studies, a direct comparison with this work is not possible.

We can compare our results to studies of CO adsorption on Pd films on W(100) [12] and W(110) [12,13]. The magnitude of the reduction in the CO-Pd bond energy seen here for a Pd monolayer on Mo(100) is comparable to that seen for W(100) [12] and W(110) [12,13]. Zhao et al. [13] performed equilibrium adsorption experiments and obtained isosteric heats of adsorption for CO on the Pd monolayer on W(110). The heat of adsorption of CO, \( \Delta H_{\text{ads}} \), is initially 20.5 kcal/mol and decreases with increasing CO coverage reaching 12.7 kcal/mol near saturation CO coverage. These authors also performed isothermal desorption
experiments and obtained the desorption energy, $E_{\text{des}}$, for CO. At low coverages $E_{\text{des}}$ was larger than $\Delta H_{\text{ads}}$ but $E_{\text{des}}$ was smaller than $\Delta H_{\text{ads}}$ at higher CO coverages. For the high CO coverages, this was explained by decreases in the sticking probability with increasing temperature. At low CO coverage it was suggested that the high values of $E_{\text{des}}$ were due to non-equilibrium effects possibly due to changes in the surface morphology. This agrees with our results using TPD which also suggest changes in the Pd film structure for Pd films on Mo(100).

On W(110) and W(100), CO desorption from thick Pd films does not resemble CO desorption from bulk Pd(111) or Pd(100) [12]. This was attributed to the formation of three-dimensional Pd islands on W(110) since there is a low temperature CO TPD state representative of desorption from the monolayer and a high temperature shoulder. This was not the case for Pd/W(100) since the CO desorption peak maximum shift was only from 305 to 370 K for Pd films 1 to 4.8 layers thick. This is well below the peak temperature for CO desorption on Pd films 5 five layers thick in our present work on Mo(100) and is also a much lower temperature than CO desorption from bulk Pd. We offer several proposals to explain this observation on W(100). First, the W(100) substrate may perturb the Pd overlayers over a longer distance than other substrates studied. Second, much larger crystallites may form and thus contribute little to the CO TPD spectra. Finally, the Pd coverage determination on W(100) may be inaccurate. These issues deserve further study.

Somewhat larger reductions in the CO-Pd bond energy have been observed on a Pd monolayer on Nb(110) [14] and Ta(110) [15,16]. On these substrates the desorption energy is 15 and 14.4 kcal/mol, respectively. This is interesting since the pseudomorphic Pd monolayer on these substrates (bcc(110)) has less lattice strain than the pseudomorphic Pd monolayer on Mo(100) (bcc(100)).
the increase in strain does not correlate simply with the reduction in the CO-Pd bond energy. However, this does not necessarily imply that lattice strain is not important. There may be some threshold Pd-Pd distance beyond which a large change in the Pd electronic structure, and thus a reduction in the CO-Pd bond energy, occurs. All of the systems studied thus far may be above this threshold, and little additional change occurs with increasing lattice strain. This possibility is also worth pursuing.

Photoemission studies of Pd monolayers on Nb(110) and Ta(110) have shown that the electronic structure of the Pd overlayer resembles a Group IB metal (Cu, Ag, Au) in that the d-band is narrowed and shifted to higher binding energies and the density of states (DOS) at the Fermi level is reduced [25-29]. Theoretical calculations by Kumar and Bennemann [30] predict that the Pd monolayer d states are more filled relative to Pd(111). On Cu [31], Ag [32] and Au [33], CO desorption occurs with energies below 17 kcal/mol. The similarities between CO desorption energetics on the Pd monolayer and these noble metals suggest that the weakened CO bonding is due to the altered electronic structure of the Pd overlayer. According to the traditional Blyholder model [34,35], CO adsorption on transition metal surfaces involves donation of electron density from the CO 5σ orbital into empty dσ states of the metal and a back-donation of electron density from the occupied metal dπ states to the CO 2π* orbital. Fewer d holes for Pd in the monolayer relative to bulk Pd makes donation from the CO 5σ orbital to the metal d states less efficient. Additionally, the shift in the Pd d-band to higher binding energy increases the separation between the occupied d states of the metal and the CO 2π* orbital of CO, leading to a reduction in back bonding to CO. Together, these effects will lead to an overall reduction in the CO-Pd bond strength on the Pd monolayer compared to bulk Pd.
While no photoemission studies have been carried out for the Pd/Mo(100) system, electronic structure changes similar to those above could be responsible for the observed effects on CO chemisorption properties. Nb, Ta, Mo, and W all form alloys with Pd [36] and these alloys may resemble intermetallic compounds. Thus, extensive bonding interactions can be expected between the Pd film and the substrate in all cases. In addition to lattice strain effects, direct Pd-substrate interactions may cause the surface electronic structure to be affected and perturb the bonding of CO as described above.

4.5 Summary

Ultrathin Pd films on a Mo(100) substrate show modified CO chemisorption properties when compared to bulk Pd(100). The largest change occurs for the pseudomorphic Pd monolayer which has a 45% decrease in the CO adsorption energy, a 34% decrease in the CO sticking probability and also shows a facile adsorption of CO into atop sites. The CO chemisorption properties can be controlled by varying the Pd film thickness over a range of at least several layers. Pd films on W(100), W(110), Ta(110) and Nb(110) show similar reductions in the Pd-CO bond energy although the effect is somewhat larger on Nb(110) and Ta(110). The increased lattice mismatch for the Pd/Mo(100) system relative to Pd/Nb(110) and Pd/Ta(110) does not lead to any additional decrease in the Pd-CO bond energy on the Pd films.
REFERENCES FOR CHAPTER IV


[11] The surface atom density of Pd(111) is $1.53 \times 10^{15}$, for Nb(110) and Ta(110) it is $1.30 \times 10^{15}$, for W(110) and Mo(110) it is $1.42 \times 10^{15}$, for Pd(100) $1.32 \times 10^{15}$, for W(100) it is $1.00 \times 10^{15}$ and for Mo(100) $1.01 \times 10^{15}$.


[16] A. Sellidj and B. E. Koel, to be published


[18] It is possible that these states are due to defect sites in the Pd film. We believe that this is highly unlikely since i) we know that the back of the crystal contributes an appreciable signal because it is highly cleaned by the electron beam heating procedure, and ii) we find that Pd adatoms strongly modify the
bonding of CO to Mo(100) at $\theta_{pd} < 1$ and therefore defect sites would have shifted TPD peak positions

[33] The heat of adsorption of CO on Au(111) is very small, less than 6 kcal/mol.; experiments by J. Hrbek showed no measurable adsorption of CO on Au(111) at 85 K under UHV conditions (personal communication).
5.1 Introduction

It is widely accepted that the properties of a catalyst are strongly influenced by the morphology and particle size of the active metal and this is therefore an important consideration in catalyst design. One interesting question is whether hydrogen is able to populate subsurface sites on very small metal clusters and the effect of cluster size. This is important since subsurface hydrogen can influence the binding energy and reactivity of adsorbates on the surface. While Leary et al. have shown that penetration of hydrogen into subsurface sites occurs for a silica-supported palladium catalyst [1] no information on the effect of particle size on this phenomenon is available.

Ultrathin Pd films (monolayer, bilayer, trilayer, etc.) can be used to probe some effects of cluster size on the penetration of hydrogen into subsurface sites by carefully controlling the Pd film thickness. Previous work by Strongin and coworkers [2-4] showed changes in the hydrogen uptake for thin Pd films on Nb and Ta due to Pd film thickness. Using resistivity measurements, they found that a Pd layer less than one monolayer thick either did not change or would inhibit hydrogen absorption in Nb and Ta. Pd films thicker than one monolayer enhanced the hydrogen uptake rate. Combining the surface properties of Pd with the bulk properties of Nb, they concluded that the barrier for hydrogen migration into the bulk of Nb was reduced and this lead to an order of magnitude increase in the solution rate.
More recently using TPD, very brief observations of hydrogen adsorption on thin Pd films on Nb(110) [5] and Ta(110) [6] have been made. A monolayer Pd film on Ta(110) decreases the H$_2$ uptake, while a Pd monolayer on Nb(110) has almost no effect when compared to the respective substrates. Hydrogen uptake increases as the Pd film thickness increases in agreement with previous observations [2-4]. The H$_2$ desorption temperature in TPD measured for a monolayer Pd film on Ta is 1400 K. By comparison, chemisorbed H$_2$ desorbs from bulk Pd(111) at about 310 K and a low temperature hydride state desorbs at 190 K [7]. No desorption peaks characteristic of H$_2$ desorption from subsurface Pd sites were seen for monolayer Pd films on Nb and Ta. On W(110) a small TPD peak at approximately 200 K was observed for Pd films equal to or exceeding one monolayer and was attributed to hydrogen desorption from a hydride phase [8]. For W(100) no well developed Pd hydride state was observed but a small shoulder at 200 K was attributed to Pd-hydride formation for a 4.8 monolayer thick film [8].

In this chapter results are presented for an investigation of hydrogen adsorption on ultrathin films of Pd on Mo(100). We show that thin Pd films on Mo(100) exhibit altered H$_2$ chemisorption properties when compared to bulk Pd(100). This is demonstrated by the absence of a Pd hydride state for Pd films less than 5 monolayers thick and a small decrease in the bond energy for the Pd-H bond for hydrogen chemisorbed on the Pd monolayer when compared to hydrogen chemisorbed on bulk Pd(100).

### 5.2 Experimental Information

The experimental apparatus used is described in chapter II. The base pressure of the chamber was $5 \times 10^{-11}$ torr. All Pd coverages $\theta_{\text{Pd}}$ are referenced to the clean Mo(100) surface, with $\theta_{\text{Pd}} = 1$ corresponding to a Pd coverage equal to the Mo(100) surface atom density, as described in chapter III. Reported H$_2$ exposures
have not been corrected for ion gauge sensitivities nor doser enhancement factor. All H₂ adsorption experiments were performed on Pd films which had been pre-annealed to 450 K in order to minimize any changes in the Pd film structure during subsequent annealing or TPD measurements. H₂ TPD experiments were carried out in line-of-sight of an apertured mass spectrometer ionizer and used a heating rate of 6 K/sec.

5.3 Results

H₂ TPD spectra obtained after large H₂ exposures (2.4 L) on several thin Pd films on Mo(100) at 150 K are shown in figure 5.1. For comparison, H₂ desorption after the same H₂ exposure on a clean Mo(100) surface at 150 K is also shown (θ_Pd = 0 curve). This exposure resulted in a saturation coverage of adsorbed hydrogen on the Mo(100) surface (θ_{H}^{sat} = 2.12 \times 10^{15} \text{ H atoms/cm}^2 [9]). Three distinct H₂ desorption peaks can be seen on the Mo(100) surface at 287, 325 and 410 K in good agreement with previous work [9,10]. These peaks begin to decrease in magnitude as Pd is deposited on the surface, with the state at 325 K disappearing by θ_Pd = 0.5 and the states at 287 and 410 K reaching a constant size for the nearly monolayer Pd film (θ_Pd = 0.9) shown in fig. 5.1. Only a small H₂ desorption feature near 290 K can be attributed to the monolayer Pd film and we designate this state β in fig. 5.1. This feature overlaps the desorption state at 287 K which is due to desorption from the clean edges and back of the Mo(100) crystal. The desorption state seen at 410 K for the θ_Pd = 0.9 film can also be attributed to desorption from the back and edges of the crystal. This is reasonable in spite of their relatively large contribution to the TPD signal since they are thoroughly cleaned by the electron beam heating technique. Since no desorption from Pd occurs at 410 K we have attempted to estimate the contribution from the Mo(100) crystal back and edges by normalizing a TPD spectrum from clean Mo(100) so that the peak at 410 K
Figure 5.1  \( \text{H}_2 \) TPD spectra as a function of Pd film thickness on Mo(100). The \( \theta_{\text{Pd}} = 0.9 \) film and the \( \theta_{\text{Pd}} \geq 20 \) film are shown by the thick lines. The dashed line represents a scaled TPD spectrum from clean Mo(100).
is the same size as that seen for the $\theta_{\text{Pd}} = 0.9$ film. The dashed curve in fig. 5.1 shows the result which clearly indicates an overlapping desorption state from the $\theta_{\text{Pd}} = 1$ film at 290 K. We can make a crude estimate of the activation energy $E_a$ for H$_2$ desorption from the monolayer film by using Redhead analysis [11]. Assuming second order kinetics and a preexponential of $1 \times 10^{-2}$ cm$^2$ s$^{-1}$, we estimate that $E_a = 18$ kcal/mol. A small increase in the size of this peak is observed as $\theta_{\text{Pd}}$ increases to 3.6. The $\beta$ state increases in size and broadens towards higher temperatures for $\theta_{\text{Pd}} = 5.5$. As $\theta_{\text{Pd}}$ increases further, this peak continues to shift towards higher temperature, and has a distinct peak temperature at 335 K for thick films ($\theta_{\text{Pd}} \geq 20$). We estimate that $E_a = 20$ kcal/mol for desorption from the $\beta$ state on the thick ($\theta_{\text{Pd}} \geq 20$) Pd film using the same assumptions as above.

A striking change in the TPD spectra occurs at $\theta_{\text{Pd}} = 5.5$ with the appearance of a new low temperature desorption peak near 190 K designated as $\alpha$ in fig. 5.1. The $\alpha$ state increases in size with $\theta_{\text{Pd}}$ and takes on a peak shape characteristic of zero order desorption and eventually becomes the dominant H$_2$ desorption channel for thicker Pd films. The desorption states at 190 and 335 K can be assigned to desorption of hydrogen from a hydride phase and from chemisorbed hydrogen on the Pd films, respectively. These peaks correspond well to the H$_2$ desorption states from bulk Pd [7,12].

Figure 5.2 shows the H$_2$ TPD area of the $\beta$ state, the H$_2$ TPD area of the $\alpha$ state, and the total H$_2$ TPD area as a function of Pd film thickness. Due to the desorption from Mo, it is difficult to accurately quantify the amount of chemisorbed H$_2$ on the Pd films. However, by assuming that the peak at 410 K is due solely to desorption from Mo we can scale the TPD spectrum from the clean Mo(100) surface as described above and subtract its TPD area from the values obtained for the $\beta$ state. The values shown in fig. 5.2 have been obtained in this manner. The H$_2$
Figure 5.2  TPD area of the $\alpha$ state, $\beta$ state, and total TPD area as a function of Pd film thickness.
TPD area of $\beta$ state is a minimum at $\theta_{\text{Pd}} = 0.9$. This state slowly increases in size and saturates at a Pd thickness of $\theta_{\text{Pd}} = 5.5$. At this Pd coverage the $\alpha$ state begins to be populated. As the Pd film thickness increases further, the H$_2$ TPD area of the $\alpha$ state continues to increase. At $\theta_{\text{Pd}} \geq 20$, the total H$_2$ TPD area is more than 2 times larger than the H$_2$ TPD area from clean Mo(100).

We estimate the amount of hydrogen desorbed from the chemisorption state on Pd increases by 48\% as $\theta_{\text{Pd}}$ increases from $\theta_{\text{Pd}} = 1$ to $\theta_{\text{Pd}} \geq 20$. This increase is not likely due to increased surface roughness as our previous studies of CO adsorption on the same Pd films on Mo(100) show only a 10\% increase in the CO TPD area for saturation exposures as the Pd film becomes thicker [13]. AES studies are also inconsistent with an extremely rough surface [14]. Instead, we propose that the dissociative sticking coefficient, $S$, for H$_2$ on Pd is decreased on the $\theta_{\text{Pd}} = 0.9$ film. Relative to the $\theta_{\text{Pd}} \geq 20$ film $S$ is decreased by 32\% for the Pd monolayer.

### 5.4 Discussion

The H$_2$ chemisorption properties of a Pd surface can be changed extensively from that of bulk Pd crystals by preparing ultrathin Pd films on Mo(100). The pseudomorphic Pd monolayer shows the largest differences, and the H$_2$ chemisorption properties may be controlled by changing the Pd film thickness.

A Pd monolayer on Mo(100) is largely inert to H$_2$ adsorption at 150 K, populating a chemisorption state with a desorption temperature of about 290 K with a relatively low sticking coefficient. Thicker Pd films also have a reduced value of $S$, until $\theta_{\text{Pd}} \geq 5.5$. The H$_2$ TPD peak due to chemisorbed hydrogen gradually shifts up in temperature to 335 K. This indicates that the H-Pd bond strength is only reduced slightly on the Pd monolayer relative to bulk Pd(100) [12]. Once $\theta_{\text{Pd}} > 5.5$, the hydride H$_2$ desorption state begins to be populated. As the Pd film thickness increases the amount of H$_2$ desorbing from the $\alpha$ state increases and when
the Pd film thickness reaches $\theta_{\text{Pd}} \geq 20$, the $\text{H}_2$ TPD spectra resemble $\text{H}_2$ desorption from bulk Pd [7,12].

Studies of Pd films on Mo(100) by AES indicate that at 450 K the morphology of these thicker films is best represented by a flat monolayer with clusters approximately 4 layers thick [14]. As more Pd is deposited the base of the clusters expand and eventually touch, forming complete layers. Thus, $\theta_{\text{Pd}}$ represents some average thickness only. Based on this description, it appears that on Mo(100) clusters approximately 5 layers thick are required to begin to have subsurface hydrogen. As the Pd film thickness increases, the effective cluster size increases, leading to an increased population of the $\alpha$ state due to more subsurface sites being available.

A direct comparison between the $\text{H}_2$/Pd/Mo(100) and other similar Pd/substrate systems is complicated by the different film preparation procedures and $\text{H}_2$ exposure temperatures. Recent work in our lab has shown that this is critical when studying the interaction of $\text{H}_2$ with Pd films and will be discussed in chapter VIII. In all previous studies, the Pd films were annealed to at least 700 K, whereas Pd films were only annealed to 450 K in this work. Structural changes are most certainly occurring in many of the systems of interest at these annealing temperatures.

Despite these complications, a comparison can be made of these results to those of $\text{H}_2$ adsorption on Pd layers on Nb(110) [5], Ta(110) [6], W(110) [8] and W(100) [8] surfaces. $\text{H}_2$ TPD spectra from monolayer films on the different substrates are different. Results presented in chapter VIII show that hydrogen desorbs from the Pd monolayer on Ta(110) mainly from a peak at 1100 K. This state is likely due to decomposition of Ta hydride at this high desorption temperature rather than Pd hydride or hydrogen chemisorbed on Pd. This is not surprising since
it is well known that Ta can dissolve large amounts of hydrogen [15]. No chemisorbed hydrogen state is seen for the Pd monolayer on Ta(110) but the $\alpha$ state is observed. The sticking coefficient for $H_2$ on the Pd monolayer on Ta(110) is small on the Pd monolayer but increases with Pd film thickness. The $\alpha$ state also increases in size as the Pd film thickness increases, similar to the results for Pd/Mo(100). For Nb(110) an increase in the hydrogen uptake is also observed as the Pd film thickness is increased [5].

On a W(110) surface, $H_2$ TPD from a monolayer Pd film showed the presence of a chemisorbed hydrogen state, which desorbed at a higher temperature (400 K) than the chemisorbed state for $H_2$ adsorbed on Pd(111), and a high temperature state (510 K) ascribed to interfacial hydrogen [8]. As the Pd film thickness was increased, the intensity of the chemisorbed $H_2$ state decreased and two new states were observed at 200 and 275 K. These were attributed to desorption of $H_2$ from a hydride phase and the surface of three dimensional clusters of Pd, respectively. For a Pd monolayer on W(100) an interfacial $H_2$ desorption state was observed at 525 K and a chemisorbed state was seen at 350 K [8]. As the Pd film thickness increases the chemisorption state shifts down in temperature to 300 K. No well developed Pd-hydride state was observed but a small shoulder at 200 K was attributed to Pd-hydride formation for films thicker than one monolayer.

The lower value of $S$ observed for the $\theta_{Pd} = 1$ film compared to thick ($\theta \geq 20$) films is similar to the results obtained for Nb and Ta [2-6] although not as dramatic. As discussed in chapter I, photoemission studies of monolayer Pd films on Nb(110) and Ta(110) show a reduction in the density of states (DOS) at the Fermi level and a narrowing of the d-band, which is shifted to higher binding energy [16-20]. It has been suggested that the electronic structure of the Pd monolayer resembles that of a noble metal [17]. For Cu [21], Ag [22], and Au [23] it is known
that H₂ chemisorption is an activated process which results in a low sticking coefficient. This is thought to be due to the lack of d holes for these metals which serve to reduce the Pauli repulsion through s-d transfer [24]. Because the d bands of Cu, Ag and Au are filled, s-d rehybridization cannot occur which causes the Pauli repulsion to be high creating an activation barrier for chemisorption. A similar situation could be occurring for the Pd monolayer films on these refractory substrates.

It appears that an effective cluster thickness of 5 layers is not generally required to populate the α state. It is visible at one monolayer Pd coverage on W(110) [8] and Ta(110) [15]. W(100) and Mo(100) may be similar in the need for a 5 layer Pd film to populate a Pd hydride state. However, we note here, and discuss more fully in chapter VIII, that the Pd film preparation procedure influences the structure of the Pd films. This is shown to cause dramatic changes in the population of the α state for Pd films on Ta(110) indicating that further investigation of the Pd film structure is required.

5.5 Summary

We have observed a decreased sticking coefficient for H₂ adsorption on the Pd monolayer at 150 K relative to thick (θ_p ≳ 20) Pd films. A Pd film thickness of greater than 5 layers was required to populate the low temperature hydride state. Films thicker than θ_p = 5.5 have H₂ adsorption properties which resemble bulk Pd surfaces.
REFERENCES FOR CHAPTER V


CHAPTER VI

CHEMISORPTION OF ETHYLENE AND ACETYLENE ON ULTRATHIN Pd FILMS ON Mo(100)

6.1 Introduction

Previous studies of the chemisorption properties of ultrathin films of metals have focused on CO adsorption. While the CO adsorption energy on these films is often decreased, CO, as a strong \( \pi \)-acceptor, probes only one aspect of the chemistry of these films. We report here the first detailed study on thin metal films of two unsaturated hydrocarbons, \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_2 \), which bond to the surface as \( \sigma \)-donors. We show that thin Pd films on Mo(100) exhibit altered chemisorption properties for \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_2 \) when compared to chemisorption on bulk Pd(100). This is demonstrated by a decrease in the amount of decomposition and rehybridization of ethylene and complex TPD spectra for acetylene.

6.2 Experimental Information

The experimental apparatus has been described in chapter II. The base pressure of the chamber was \( 5 \times 10^{-11} \) torr. All Pd coverages are referenced to the clean Mo(100) surface, with \( \theta_{\text{pd}} = 1 \) corresponding to a Pd coverage equal to the Mo(100) surface atom density, as described in chapter III. All adsorption experiments were performed on Pd films which had been annealed to 450 K in order to minimize any changes in the Pd film structure during subsequent annealing or TPD experiments. The heating rate during TPD experiments was 6 K/sec. HREELS experiments were performed in the specular direction with a beam energy
of 2.8 eV. The resolution varied between 70 and 86 cm$^{-1}$. All HREELS spectra were recorded at 100 K.

6.3 Results

6.3.1 Ethylene (C$_2$H$_4$) Adsorption

Ethylene TPD spectra following large C$_2$H$_4$ exposure (2.4 L) at 150 K are shown in figure 6.1 as a function of Pd film thickness. This exposure gave a saturation coverage of C$_2$H$_4$ on the clean Mo(100) surface. Mass to charge ratios of 2, 27, and 28 were monitored during TPD experiments. On the $\theta_{\text{Pd}} = 0.9$ film a single molecular C$_2$H$_4$ desorption state is seen at 247 K. Using Redhead analysis [1], the activation energy for molecular C$_2$H$_4$ desorption is found to be 15 kcal/mol assuming first order kinetics and a preexponential of $10^{13}$. As the Pd coverage increases this peak shifts to slightly higher temperature and appears at 279 K for $\theta_{\text{Pd}} = 5.1$. At a Pd thickness of $\geq$ 20 layers a second peak appears on the high temperature side of this peak at 287 K. This TPD spectrum has peak temperatures close to that obtained for C$_2$H$_4$ desorption from Pd(100) although the relative intensity of the low temperature state on the thick Pd film is somewhat larger than that obtained from C$_2$H$_4$ desorption from bulk Pd(100) [2]. On the thick film, Redhead analysis yields an activation energy for C$_2$H$_4$ desorption of 17 kcal/mol under the same assumptions mentioned above. This shows C$_2$H$_4$ to be slightly more weakly bound to the Pd monolayer than to the thick ($\geq$ 20 layers) Pd film.

Figure 6.2 shows H$_2$ TPD spectra following saturation C$_2$H$_4$ exposures at 150 K as a function of Pd film thickness. These spectra were taken concurrently with the C$_2$H$_4$ TPD spectra shown in Fig. 6.1. On the $\theta_{\text{Pd}} = 0.9$ film a H$_2$ desorption state at 316 K is observed with a small shoulder due to desorption from clean Mo(100) at 350 K. At $\theta_{\text{Pd}} = 2.4$ the low temperature peak begins to increase.
Figure 6.1  \( \text{C}_2\text{H}_4 \) TPD spectra from several Pd films following 2.4 L \( \text{C}_2\text{H}_4 \) exposures at 150 K.
Figure 6.2 H₂ TPD spectra from several Pd films following 2.4 L C₂H₄ exposures at 150 K.
in size and a new state begins to be visible as a shoulder at 400 K. As $\theta_{pd}$ increases
the low temperature peak continues to grow larger and the new high temperature
peak grows and shifts up to 460 K. On the 20 layer thick film hydrogen desorption
after ethylene exposure resembles that from C$_2$H$_4$ exposure on bulk Pd(100) [2],
although the peak maxima appear at lower temperatures on the Pd film, the relative
intensities of the two peaks are comparable. By comparison, hydrogen desorption
from H$_2$ chemisorbed on the thin Pd films occurs in a temperature range from 200 to
400 K. Because of this we assign the H$_2$ TPD peak at 460 K to decomposition rate
limited desorption. If we assume second order desorption kinetics and a
preexponential of $1 \times 10^{-2}$ cm$^2$ s$^{-1}$, Redhead analysis gives $E_a = 28$ kcal/mol. The
peak at 306 K is likely due to a desorption rate limited process.

Figure 6.3a shows the C$_2$H$_4$ TPD area as a function of Pd film thickness.
The C$_2$H$_4$ TPD area initially increases as Pd is deposited, reaches a maximum at
$\theta_{pd}$=1.4 and then slowly decreases with Pd film thickness. This shows that 20% 
more C$_2$H$_4$ desorbs from the Pd monolayer than the thick Pd film. The hydrogen
TPD area goes through a minimum at a Pd film thickness of 1.4 layers and then
slowly increases with Pd film thickness complementary to the molecular C$_2$H$_4$ TPD
area as shown in Figure 6.3b.

An HREELS spectrum of ethylene adsorbed on the Pd monolayer at 100 K
is shown in figure 6.4. Peaks in the loss spectrum are observed at 2980 cm$^{-1}$, 1525
cm$^{-1}$, 1235 cm$^{-1}$, and 865 cm$^{-1}$. These peaks are assigned as due to $v$(CH),
$\delta$(CH$_2$), $v$(CC), and CH$_2$def respectively. The energy loss assignments were
derived from comparison with ethylene adsorbed on bulk Pd(100) and are listed in
Table I. Also included in this table are values for ethylene adsorbed on bulk
Pd(100), gas phase ethylene, Zeise's salt (K[(C$_2$H$_4$)PtCl$_3$], C$_2$H$_4$Br$_2$ and
C$_2$H$_4$/Pt(111). Zeise's salt and C$_2$H$_4$Br$_2$ are included since they are models for $\pi$-
Figure 6.3  (a) C$_2$H$_4$ TPD area as a function of Pd film thickness.  (b) H$_2$ TPD area as a function of Pd film thickness.
Figure 6.4  HREELS spectrum of $\text{C}_2\text{H}_4$ adsorbed on a $\theta_{\text{Pd}} = 1.1$ film at 150 K.
<table>
<thead>
<tr>
<th>mode</th>
<th>Pd monolayer</th>
<th>bulk Pd(100)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Zeise’s salt&lt;sup&gt;b&lt;/sup&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;/Pt(111)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>gas&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>v(CH2)</td>
<td>2980</td>
<td>2980</td>
<td>3079</td>
<td>3005</td>
<td>3000</td>
<td>3026</td>
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<tr>
<td>δ(CH2)</td>
<td>1525</td>
<td>1455</td>
<td>1515</td>
<td>1420</td>
<td>1430</td>
<td>1342</td>
</tr>
<tr>
<td>v(CC)</td>
<td>1234</td>
<td>1135</td>
<td>1243</td>
<td>1019</td>
<td>1050</td>
<td>1623</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;def</td>
<td>865</td>
<td>920</td>
<td>975</td>
<td>1278</td>
<td>980</td>
<td>1023</td>
</tr>
<tr>
<td>v(PdC)</td>
<td>439</td>
<td>390</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

<sup>a</sup> [2]. <sup>b</sup>K([C<sub>2</sub>H<sub>4</sub>)PtCl<sub>3</sub>] [3]. <sup>c</sup>Gauche form, A modes only [4]. <sup>d</sup> [5]. <sup>e</sup>A<sub>1</sub> modes only [6].
bonded and di-\(\sigma\) bonded ethylene and \(\text{C}_2\text{H}_4/\text{Pt}(111)\) is included since it is known to be di-\(\sigma\) bonded. By comparing the observed values for \(\text{C}_2\text{H}_4\) on the Pd monolayer with the other values in Table I it can be seen that the vibrational energies of ethylene adsorbed on the Pd monolayer most closely resembles the vibrational energies of Zeise’s salt. This is a strong indication that ethylene is \(\pi\)-bonded on the monolayer film rather than di-\(\sigma\) bonded.

A measure of the hybridization of \(\text{C}_2\text{H}_4\) on metal surfaces is the \(\pi\sigma\) parameter [7] defined by

\[
\pi\sigma(\text{C}_2\text{H}_4) = \frac{(1623 - \text{band I})}{1623} + \frac{(1342 - \text{band II})}{1342} \times 0.366
\]

where band I refers to the higher frequency and band II to the lower frequency of the \(\nu(\text{CC}) - \delta(\text{CH}_2)\) pair. This formulation allows a comparison of the degree of rehybridization of ethylene on various surfaces. Table II lists the \(\pi\sigma\) parameter for several surfaces.

<table>
<thead>
<tr>
<th>System</th>
<th>(\pi\sigma) Parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_4\text{Br}_2)</td>
<td>1.0</td>
<td>4</td>
</tr>
<tr>
<td>(\text{Pt}(111))</td>
<td>0.92</td>
<td>5</td>
</tr>
<tr>
<td>(\text{Ni}(100))</td>
<td>0.83</td>
<td>8</td>
</tr>
<tr>
<td>(\text{Pd}(100))</td>
<td>0.78</td>
<td>7</td>
</tr>
<tr>
<td>(\text{Pd}(111))</td>
<td>0.43</td>
<td>9</td>
</tr>
<tr>
<td>(\text{Pd/Mo}(100))</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Zeise’s Salt</td>
<td>0.38</td>
<td>3</td>
</tr>
<tr>
<td>(\text{Cu}(100))</td>
<td>0.21</td>
<td>10</td>
</tr>
<tr>
<td>(\text{Ag}(110) + \text{O})</td>
<td>0.14</td>
<td>11</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_4) gas</td>
<td>0.0</td>
<td>6</td>
</tr>
</tbody>
</table>
This parameter is zero for gas phase $\text{C}_2\text{H}_4$, 0.38 for Zeise's salt and unity for $\text{C}_2\text{H}_4\text{Br}_2$. For ethylene adsorbed on the Pd monolayer, $\pi\sigma(\text{C}_2\text{H}_4) = 0.39$ whereas on bulk Pd(100) $\pi\sigma(\text{C}_2\text{H}_4) = 0.78$ [7]. This indicates that considerably less rehybridization of $\text{C}_2\text{H}_4$ from sp$^2$ to sp$^3$ occurs on the monolayer relative to bulk Pd(100). Since $\pi$-bonded ethylene has been shown to be less likely to decompose on Pd(100) [2] it is expected that less ethylene would decompose on the monolayer than on thick films. This is consistent with the TPD data presented above.

6.3.2 Acetylene (C$_2$H$_2$) Adsorption

Acetylene TPD spectra following large $\text{C}_2\text{D}_2$ exposures (2.4 L) at 150 K are shown in figure 6.5 as a function of $\theta_{\text{Pd}}$. This exposure resulted in saturation $\text{C}_2\text{D}_2$ coverages on the clean Mo(100) surface. On the monolayer Pd film desorption of acetylene has a two peak structure with peak maxima at 258 and 349 K. This is similar to acetylene desorption from bulk Pd(100) where a broad plateau extending from 188 to 350 K is observed [12]. By $\theta_{\text{Pd}} = 3$, the high temperature peak has disappeared and the low temperature peak has shifted to 244 K. This peak continues to shift down in temperature reaching a final value of 235 K for a Pd film thickness of 20 layers.

$\text{D}_2$ desorption was also monitored during TPD experiments following saturation $\text{C}_2\text{D}_2$ exposures (2.4 L) on the Pd films. This is shown in Fig. 6.6. The TPD spectrum of $\text{D}_2$ desorbing from the Pd monolayer has two peaks with maxima at 328 and 443 K and a long plateau extending to 637 K. This has the general shape and temperature range for hydrogen desorption from bulk Pd(100) following $\text{C}_2\text{H}_2$ exposures although the onset temperature for hydrogen desorption is lower on the Pd monolayer and there is only one peak followed by a long plateau on bulk Pd(100) [12]. As the Pd thickness increases the $\text{D}_2$ TPD spectra change continuously. The onset of desorption becomes more abrupt, the peak initially at...
Figure 6.5  C$_2$D$_2$ TPD spectra from several Pd films following 2.4 L C$_2$D$_2$ exposures at 150 K.
Figure 6.6 D₂ TPD spectra from several Pd films following 2.4 L C₂D₂ exposures at 150 K.
328 K shifts down to 256 K and new states are seen at 399 and 488 K. Thus, for acetylene TPD, the Pd monolayer resembles Pd(100) single crystals while thicker films have TPD spectra "rich in structure".

Figure 6.7 shows vibrational spectra of C$_2$D$_2$ and C$_2$H$_2$ on a Pd monolayer. The mode assignments are listed in Table III and are confirmed by isotope shifts. Also shown in Table III are the vibrational frequencies for surface species formed from C$_2$D$_2$ and C$_2$H$_2$ adsorption on a Pd(100) single crystal at 300 K [13]. The observed vibrational frequencies of C$_2$H$_2$ on the $\theta_{pd} = 1$ film on Mo(100) are attributed to strongly rehybridized acetylene as evidenced by the low $v_{CH}$ frequency and $v_{CC}$ frequency at 2956 and 1231 cm$^{-1}$ respectively. Only small shifts in the position of the HREELS peaks are observed upon adsorption of C$_2$H$_2$ on a Pd monolayer when compared to bulk Pd(100). This indicates that, unlike ethylene, the extent of rehybridization is nearly the same for acetylene on a Pd monolayer on Mo(100) as it is for C$_2$H$_2$ on bulk Pd(100). An HREELS spectrum of a saturation exposure (2.4 L) of C$_2$H$_2$ on a thick Pd film is also shown in fig. 6.8 and compares well to the Pd monolayer. All vibrational frequencies seen here on the thick Pd film ($\theta_{pd} \geq 20$) are in good agreement with previously reported values for C$_2$H$_2$ on bulk Pd(100) [13].

6.4 Discussion

The chemisorption properties of Pd for ethylene can be changed extensively from bulk Pd(100) properties by making ultrathin films on Mo(100). The Pd monolayer always shows the largest differences, and it appears that some of the film properties can be "tuned" or varied by changing the Pd film thickness. However, acetylene is less affected. The details for each of the adsorbates will now be considered.
Figure 6.7 HREELS spectrum of C₂H₂ adsorbed on a θ_{Pd} = 1.1 film and a θ_{Pd} ≥ 20 film at 150 K. Also shown is an HREELS spectrum of C₂D₂ on a θ_{Pd} = 1.1 film (bottom spectrum).
Table III: Vibrational Frequencies and Mode Assignments for Acetylene Species

<table>
<thead>
<tr>
<th>Mode Assignment</th>
<th>C$_2$H$_2$ on Pd Monolayer</th>
<th>C$_2$D$_2$ on Pd Monolayer</th>
<th>vH/vD</th>
<th>C$_2$H$_2$ on Thick Pd Film</th>
<th>C$_2$H$_2$ on Pd(100)$^a$</th>
<th>C$_2$D$_2$ on Pd(100)$^a$</th>
<th>vH/vD</th>
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<td>2920</td>
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</tr>
<tr>
<td>δ(CH)</td>
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<td>1168</td>
<td>1.21</td>
<td>1399</td>
<td>1390</td>
<td>a</td>
<td>-</td>
</tr>
<tr>
<td>v(CC)</td>
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<td>1210</td>
<td>1185</td>
<td>1.02</td>
</tr>
<tr>
<td>p(CH)</td>
<td>1075</td>
<td>a</td>
<td>-</td>
<td>1069</td>
<td>935</td>
<td>670</td>
<td>1.39</td>
</tr>
<tr>
<td>p(CH)</td>
<td>784</td>
<td>502</td>
<td>1.56</td>
<td>784</td>
<td>710</td>
<td>500</td>
<td>1.42</td>
</tr>
<tr>
<td>v(PdC)</td>
<td>511</td>
<td>a</td>
<td>1.01</td>
<td>511</td>
<td>a</td>
<td>a</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ [13].
Ultrathin Pd films on Mo(100) deviate from bulk Pd(100) with regard to ethylene chemisorption properties. On a monolayer Pd film the desorption peak temperature is below that observed for ethylene desorption from bulk Pd(100) indicating a slightly weaker bond to the surface. A more dramatic change is observed in the vibrational spectrum which indicates that little rehybridization from the gas phase sp² state occurs. A gradual return to bulk Pd behavior is seen as the Pd coverage increases similar to the results obtained for H₂ and CO in chapters IV and V.

The altered chemisorption properties of C₂H₄ may be explained in terms of an altered electronic structure. It is generally believed that ethylene bonding to transition metal surfaces is similar to that which occurs between π acids and transition metals in organometallic complexes [14]. Within this context, the filled C₂H₄ π orbital donates its electrons to vacant dσ orbitals of the metal while the empty C₂H₄ π* orbital accepts electrons from filled dπ orbitals of the metal. The amount of back donation is thought to be the dominating factor in determining the extent of rehybridization. It is clear from the value of the πσ parameter (0.39) that C₂H₄ is much less rehybridized on the Pd monolayer than on bulk Pd(100). We can understand this in the following way. First, if the d band of Pd in the monolayer is full [15-20] the π orbital of ethylene will be less effective at donating charge to the surface and forming a σ-donornor bond. Second, if the Pd d band is full (or even if the d orbitals of Mo and Pd are extensively involved in bonding) then it follows that the resulting Pd d band will have an overall lowering of energy. This in turn will increase the energy gap between the Pd d band of the surface and the π* orbital of C₂H₄ leading to inefficient overlap and thus little back donation. Both of these effects will weaken the C₂H₄-Pd bond. This again suggests that the Pd monolayer has chemisorption properties similar to the noble metals. However, a significant
amount of C$_2$H$_4$ still decomposes on the Pd monolayer while no decomposition is seen on Ag(111) [21]. Thus, while the chemisorption properties of ethylene on the Pd monolayer approach that of ethylene on Ag, it is clear that there are still significant differences.

The chemistry of acetylene on the Pd monolayer is similar to that on bulk Pd surfaces. Both the TPD and HREELS spectra of acetylene on the Pd monolayer closely resemble the respective spectra on Pd(100) single crystals. A possible explanation for this is that the bonding of acetylene to Pd is strong enough to rehybridize Pd in the monolayer back toward its normal bulk electronic structure, i.e., it is more favorable to make strong Pd-C bonds than to have a weak π-bonded acetylene species on a modified monolayer. As $\theta_{\text{Pd}}$ increases, the TPD spectra change. Desorption occurs over a wider temperature range and new desorption states are populated. In contrast, the HREELS spectra of chemisorbed C$_2$H$_2$ at low temperature remain nearly constant as the film thickness increases. This indicates that the initial bonding of acetylene on the thick Pd films (20 layers) is the same as on the Pd monolayer. However, the TPD results indicate that the very strong chemisorption bonding of acetylene and the hydrocarbon fragments formed from decomposition may actually change the morphology of the Pd film during TPD experiments.

6.5 Summary

We have shown that the Pd monolayer on Mo(100) has altered chemisorption properties relative to bulk Pd(100) for C$_2$H$_4$ but not for C$_2$H$_2$. This is demonstrated by a reduction in the amount of decomposition of C$_2$H$_4$ during thermal desorption and a decrease in the rehybridization of C$_2$H$_4$ upon adsorption. As the Pd thickness is increased the surface gradually acquires bulk Pd(100) properties. These observations may be a result of the bonding interaction of Pd with
the Mo(100) substrate causing a filling of the Pd d band and a shift of the d-band to higher binding energies. This causes a decrease in the overlap of the C$_2$H$_4$ $\pi^*$ orbital with the Pd d orbitals. This results in C$_2$H$_4$ being much more $\pi$ bonded to the monolayer than on bulk Pd(100). Unlike C$_2$H$_4$, C$_2$H$_2$ chemisorption is not strongly altered on the Pd thin films but TPD results suggest chemisorption induced morphology changes upon heating.
REFERENCES FOR CHAPTER VI

CHAPTER VII

THE ADSORPTION AND REACTION OF NO AND N₂O ON ULTRATHIN Pd FILMS DEPOSITED ON Ta(110)

7.1 Introduction

In the present chapter studies of NO chemisorption on ultrathin Pd films on Ta(110) are discussed. Some studies of the adsorption of N₂O were also carried out. NO was chosen for this study for several reasons. NO is a weaker \( \pi \)-acid than CO and may probe different aspects of the surface reactivity than CO. NO chemisorption is more versatile than CO chemisorption on the same surfaces, since NO can bond in a linear and bent atop geometry [1,2,3] in addition to a bridging geometry [1,2,4,5] and as "lying down" NO [6]. There has also been speculation about dimer formation on some surfaces [7,8]. Finally, from a technological viewpoint, there is an interest in the catalytic reduction of NO by transition metal surfaces due to the desire to reduce NO emissions from internal combustion engine exhaust [9,10].

7.2 Experimental Information

The apparatus used has been described in chapter II. The base pressure of the chamber was \( 1 \times 10^{-10} \) torr. Dosing of all gases was carried out with the aid of a glass capillary array with a flux enhancement of 50. Exposures are reported in units of Langmuirs (\( 1 \text{L} = 1 \times 10^{-6} \text{torr-s} \)) and are corrected for ionization gauge efficiency and doser enhancement factor. All NO and N₂O adsorption experiments were performed on Pd films which had been annealed to 600 K, unless otherwise specified, in order to avoid (as much as possible) any changes in the Pd film
structure during subsequent annealing of NO adlayers or TPD experiments. The heating rate used during TPD experiments was 5 K/sec. Pd coverages were derived from AES and LEED observations, with $\theta_{\text{Pd}} = 1$ corresponding to a Pd coverage approximately equal to the Pd(111) surface atom density [11]. HREELS experiments were performed in the specular direction with a incident electron beam energy of 4 eV. The resolution of the spectrometer varied between 60 and 85 cm$^{-1}$ and all spectra were recorded at $T \leq 100$ K.

Recently the growth and structure of Pd films on Ta(110) have been reported [11]. At room temperature, the growth is best described by a Frank-van der Merwe (layer-by-layer) growth mechanism. Initially, the first Pd layer grows in a two dimensional pseudomorphic structure, probably as islands. This continues up to $\theta_{\text{Pd}} = 0.65$. Subsequent deposition of Pd causes a structural phase transition to occur. This transition causes "beat" spots to appear in the LEED pattern that are aligned parallel to the short axis of the distorted hexagon of the substrate. The beat pattern has been attributed to the formation of fcc(111) islands [11, 12]. This leads to the formation of an fcc(111) Pd monolayer with a surface atom density approximately equal to that of bulk Pd(111). We define this Pd coverage as $\theta_{\text{Pd}} = 1.0$. As further Pd is deposited the film continues to grow with an fcc(111) structure. The beat pattern observed in LEED fades and a symmetric hexagon characteristic of the fcc(111) structure is observed. The growth of Pd on Ta(110) at 125 K is similar to that at 300 K although the growth deviates slightly from the layer-by-layer mode. Annealing experiments to probe the thermal stability of the monolayer and ultrathin Pd films on Ta(110) show that the bcc(110) pseudomorphic monolayer is stable to approximately 1350 K. The fcc(111) monolayer is stable to temperatures near 550 K. At this temperature the beat pattern begins to fade and
streaking is observed. Films thicker than this may agglomerate into three dimensional clusters two to three layers thick at temperatures as low as 370 K.

7.3 Results

7.3.1 NO Chemisorption on a Monolayer Pd Film, $\theta_{\text{Pd}} = 1$

Figures 7.1a-c show the TPD spectra following NO exposures on a $\theta_{\text{Pd}} = 1$ film at 95 K. The desorption products observed are NO, N$_2$O and N$_2$. NO exposures of 0.28 L lead to a single desorption state of NO, labeled $\alpha_1$, at 130 K (fig. 7.1a). With increasing exposure the peak maximum shifts to higher temperature reaching a value of 160 K at an NO exposure of 1.74 L. A new desorption state at 130 K, labeled $\alpha_2$, is seen for NO at this exposure. Increasing NO exposure causes both states to increase in size with the $\alpha_2$ state eventually becoming larger than the $\alpha_1$ state. Figure 7.1b shows the N$_2$O TPD spectra following NO exposures. N$_2$O desorption occurs from single state at the same temperature as the $\alpha_1$ NO desorption state throughout the entire range of NO exposures. For 225 L NO exposures a small shoulder is seen on the low temperature side of the N$_2$O desorption peak at 125 K. N$_2$ desorption also occurs at the same temperature as the $\alpha_1$ NO desorption state, as shown in fig. 7.1c. There is also a small amount of N$_2$ desorption at 350 K for some of the NO exposures. This feature was not reproducible and could not always be discerned from the background. Broadening of the desorption feature at 160 K and a large increase in the amount of N$_2$ desorbing is observed for 225 L NO exposures. This latter result is due to reaction of NO with the clean, Pd-free back and edges of the Ta(110) crystal leading to N$_2$ desorption. Separate experiments conducted on a clean Ta(110) crystal show similar TPD spectra following NO exposure.
Figure 7.1 TPD Spectra from a $\theta_{pd} = 1$ film as a function of NO exposure at 95 K. (a) NO TPD spectra (30 amu), (b) $N_2$ TPD spectra (44 amu), (c) $N_2O$ TPD spectra (28 amu).
We can quantify the relative amount of NO, N₂O and N₂ desorbing from the θₚd = 1 film by using the TPD areas. Figure 7.2 shows the TPD areas as a function of NO exposure for all three desorption products after correcting for the N₂O cracking fractions. Initially, the amount of NO, N₂O and N₂ desorbing are nearly equal. As the NO exposure is increased the desorption yield of all three desorption products increases, and their relative amounts remain approximately equal. This trend continues until the α₂ NO desorption state begins to be populated. At this point the amount of NO desorbing becomes larger than the amount of N₂O or N₂ desorbing. At an NO exposure of 140 L, a large increase in the amount of N₂ desorbing is observed, making it the dominant desorption product. As mentioned above, this is likely due to background contributions. The TPD areas of NO, N₂O and N₂ saturate by an NO exposure of 225 L.

Desorption of NO from a θₚd = 1 film can be contrasted with NO desorption from a bulk Pd(111) single crystal. Figure 7.3 shows the results of TPD experiments following NO exposures at 100 K on a Pd(111) single crystal. At low θ₈NO the high temperature state labeled β₃ is observed at 540 K. As θ₈NO increases this state grows in size and the peak maximum slowly shifts to lower temperature. Increasing the NO exposure still further causes states at 290 and 270 K to be sequentially filled. Adsorption of NO on Pd(111) is completely reversible and no desorption products other than NO are observed. HREELS experiments of NO adsorption indicate that at low θ₈NO a bridge bonded species is formed. At θ₈NO = 0.51 an atop species begins to be populated and at saturation NO coverage (θ₈NO = 0.75) the bridge bonded and atop NO species have nearly equal intensities in the HREELS spectrum.

Conversely, for a monolayer Pd film on Ta(110), a significant amount of NO decomposition is observed and all desorption occurs below 250 K. Assuming
Figure 7.2  Comparison of the NO, N$_2$O and N$_2$ TPD areas as a function of NO exposure on a $\theta_{pd} = 1$ film at 95 K.
NO TPD spectra following NO exposures on Pd(111) at 100 K from reference 2. NO exposures were a) 0.025 L, b) 0.125 L, c) 0.25 L, d) 0.075 L, e) 0.675 L, f) 0.85 L, g) 1.0 L, h) 1.2 L, i) 1.4 L, j) 4.0 L.
first order desorption kinetics and a preexponential factor of $10^{13}$, Redhead analysis [13] yields an activation energy of desorption, $E_a$, of 8 kcal/mol for the $\alpha_2$ NO desorption state and 10 kcal/mol for the $\alpha_1$ NO desorption state. A similar treatment for the three desorption states of NO on bulk Pd(111) yields activation energies of 20, 21, and 38 kcal/mol for the $\beta_1$, $\beta_2$, and $\beta_3$ states respectively (see fig. 7.3) [2].

HREELS experiments were conducted in order to identify the adsorbed species at 95 K and to identify the adsorption sites for NO on the Pd monolayer. Figure 7.4 shows these results for a $\theta_{pd} = 1$ film with increasing NO exposures at 95 K. A peak in HREELS is observed at 316 cm$^{-1}$ with two other poorly resolved peaks at 1588 and 1690 cm$^{-1}$ for a 0.28 L NO exposure. We assign these peaks to the Pd-NO stretch, $v_{PD-NO}$, and the N-O stretching mode, $v_{NO}$, for NO adsorbed in two-fold bridge sites and atop sites, respectively. These assignments are in good agreement with previous work on Pd(111) single crystals [1,2]. The peak at 1690 cm$^{-1}$ increases in intensity and shifts up to 1756 cm$^{-1}$ for a 56 L NO exposure. Very large exposures ($\geq 140$ L) of NO result in the appearance of six new peaks at 262, 622, 778, 1300, 1594 and 1870 cm$^{-1}$ indicating the formation of a new species (while the peak at 622 cm$^{-1}$ is not well developed in this particular spectrum, other spectra show a fairly strong peak in this region). This spectrum closely resembles that of N$_2$O$_3$ [14] with an additional peak at 1768 cm$^{-1}$ due to coadsorbed NO.

Table I lists the vibrational modes of N$_2$O$_3$ dissolved in CH$_2$Cl$_2$ [14], N$_2$O$_3$ adsorbed on Au(111) [15] and the peaks observed here on the Pd monolayer. It can be seen that there is excellent agreement between the peaks observed in this work and that seen for N$_2$O$_3$ dissolved in CH$_2$Cl$_2$ [14] as well as reasonable agreement with N$_2$O$_3$ adsorbed on Au(111).
Figure 7.4. HREELS spectra as a function of NO exposures on a $\theta_{Pd} = 1$ film at 95 K.
Table I: Comparison of Vibrational Frequencies for N$_2$O$_3$

<table>
<thead>
<tr>
<th>Mode</th>
<th>N$_2$O$_3$/Au(111)$^a$</th>
<th>N$_2$O$_3$ in CH$_2$Cl$_2$$^b$</th>
<th>N$_2$O$_3$/Pd Monolayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>v (O$_2$N-NO)</td>
<td>250</td>
<td>253</td>
<td>262</td>
</tr>
<tr>
<td>p (O$_2$NNO)</td>
<td>450-650</td>
<td>614</td>
<td>622</td>
</tr>
<tr>
<td>δ (NO$_2$)</td>
<td>800</td>
<td>772</td>
<td>778</td>
</tr>
<tr>
<td>v$_s$ (NO$_2$)</td>
<td>1180</td>
<td>1291</td>
<td>1300</td>
</tr>
<tr>
<td>v$_a$ (NO$_2$)</td>
<td>1270</td>
<td>1600</td>
<td>1594</td>
</tr>
<tr>
<td>v (NO)</td>
<td>1890</td>
<td>1849</td>
<td>1858-1870</td>
</tr>
</tbody>
</table>

$^a$ [15], $^b$ [14]

It is possible that an N$_2$O$_3$ impurity contributes to the HREELS spectrum at these high exposures. However, N$_2$O$_3$ is extensively dissociated into NO and N$_2$O in the gas phase making this unlikely [16]. Additionally, if an N$_2$O$_3$ impurity was present in the NO we would expect multilayer formation at 95 K which would show up both in HREELS and TPD. No sign of multilayer formation is observed. An alternative explanation for the observation of N$_2$O$_3$ is that we are running a low probability reaction on the surface at these very high exposures.

HREELS experiments were also conducted for several initial NO coverages as a function of annealing temperature. Figure 7.5 shows an annealing series for an NO exposure of 0.28 L. At 95 K, peaks at 328, 1588 and 1690 cm$^{-1}$ are seen as discussed above. An additional peak at 2062 cm$^{-1}$ due to the adsorption of CO from the background is also present. Upon heating the surface to 125 K all peaks disappear except for the peak due to adsorption of CO from the background. For a 56 L NO exposure, peaks are seen at 328, 1588 and 1756 cm$^{-1}$ at 95 K, as shown in Fig. 7.6. A small shift to 1738 cm$^{-1}$ is observed for v$_{\text{NO}}$ for NO adsorbed in atop
Figure 7.5  HREELS spectra following a 0.28 L NO exposure on the Pd monolayer at 95 K and after annealing to 125 K.
Figure 7.6 HREELS spectra following a 56 L NO exposure on the Pd monolayer at 95 K and after annealing to the specified temperature.
sites upon annealing to 125 K. Annealing to 150 K causes $v_{\text{NO}}$ for NO adsorbed in atop sites to shift to 1648 cm$^{-1}$ and decrease in intensity and also causes $v_{\text{NO}}$ due to NO adsorbed in two-fold bridging sites to disappear. This peak shifts down to 1606 cm$^{-1}$ and a new, broad feature emerges at 682 cm$^{-1}$ when annealing at 175 K. $v_{\text{NO}}$ is no longer detectable but small peaks are seen at 358 and 682 cm$^{-1}$ after annealing to 250 K. These peaks are likely due to nitrogen and oxygen atoms adsorbed on the surface since these species are detected by AES.

Figure 7.7 shows an annealing series for an initial exposure of 224 L NO on the $\theta_{\text{pd}} = 1$ film at 95 K. At 95 K an HREELS spectrum attributed to $\text{N}_2\text{O}_3$ coadsorbed with NO is observed as discussed above. Annealing to 125 K produces a spectrum with peaks at 280, 658, 1270 and 1828 cm$^{-1}$. After annealing to 175 K, a broad feature near 720 cm$^{-1}$ is observed and a peak at 1930 cm$^{-1}$ appears. This latter peak is attributed to NO since a peak at 1930 cm$^{-1}$ was attributed to NO on Ag(110) [17], but could be due to CO adsorption from background gas. Only one weak peak is seen near 800 cm$^{-1}$ after heating to 350 K and annealing to 900 K leads to the disappearance of all peaks.

Exposing NO on a $\theta_{\text{pd}} = 1$ film (showing the beat pattern in LEED observations) at 95 K initially caused only an increase in the background intensity, which increased with NO coverage. The beat pattern was visible for NO exposures up to 1.2 L but eventually all spots were obscured, including those due to the substrate. This shows conclusively that NO chemisorption, in contrast to CO adsorption [18], disrupts the Pd monolayer film structure and disorders the surface at 95 K. The surface was then annealed to successively higher temperatures. Spots corresponding to the beat pattern reappeared at 400 K but were very weak. No other ordered patterns were ever observed.
Figure 7.7  HREELS spectra following a 224 L NO exposure on the Pd monolayer at 95 K and after annealing to the specified temperature.
7.3.2 NO Chemisorption on Pd Films of Increasing Thickness

Thermal desorption spectra following very small (0.54 L) NO exposures on Pd films at 95 K are shown in figs. 7.8a - c as a function of Pd film thickness. The $\theta_{Pd} = 0.73$ film is the pseudomorphic bcc(110) monolayer. On this surface a single desorption state is seen for NO with a peak maximum at 135 K (fig. 7.8a). Increasing the Pd film thickness from $\theta_{Pd} = 0.73$ to $\theta_{Pd} = 1.07$ (to form the incommensurate fcc(111) Pd monolayer) causes no change in the NO TPD spectrum. For a Pd coverage of $\theta_{Pd} = 2.02$ the amount of NO desorption has decreased substantially without a change in the desorption temperature. Increasing the Pd film thickness to $\theta_{Pd} = 3.18$ causes a further decrease in the amount of NO desorbing from the peak at 135 K while a new peak is observed at 480 K, with a broad feature at 370 K. The amount of NO desorbing from the $\theta_{Pd} = 3.18$ film is approximately five times that desorbing from the $\theta_{Pd} = 1.07$ film. Finally, on the $\theta_{Pd} = 5$ film, an NO desorption state with a peak maximum of 480 K and a small shoulder at 350 K is in good agreement with previously reported NO desorption from bulk Pd(111) for low NO coverages [2].

Figure 7.8b shows corresponding TPD spectra of N$_2$O following 0.54 L NO exposures as a function of Pd film thickness. N$_2$O desorbs from a single state at 135 K on the $\theta_{Pd} = 0.73$ film. Similar to NO, there is no change in the TPD spectrum of N$_2$O when the film thickness is increased to $\theta_{Pd} = 1.07$. As the Pd film thickness is increased further, the amount of N$_2$O desorbing decreases without a change in the desorption temperature and no N$_2$O desorbs from the $\theta_{Pd} = 5$ film.

N$_2$ TPD spectra following 0.54 L NO exposures as a function of $\theta_{Pd}$ are shown in fig. 7.8c. A major desorption state is seen for N$_2$ at 135 K, with a small amount desorbing near 350 K on the $\theta_{Pd} = 0.73$ film. There are no significant changes in the TPD spectrum when the film thickness is increased to $\theta_{Pd} = 1.07$. For a Pd film thickness of $\theta_{Pd} = 2.02$, the amount of N$_2$ desorbing from the 135 K
Figure 7.8 TPD spectra following 0.54 L NO exposures at 95 K as a function of Pd film thickness.
(a) NO TPD spectra (30 amu), (b) N$_2$O TPD spectra (44 amu), (c) N$_2$ TPD spectra (28 amu).
desorption state has decreased and a small shoulder has developed on its high temperature side at 200 K. The desorption feature initially at 350 K has shifted up to 400 K and increased in size. Increasing the Pd film thickness further causes the N₂ desorption state at 135 K to decrease further while the states at 200 and 400 K broaden and shift towards higher temperatures. On the \( \theta_{pd} = 5 \) film N₂ desorption occurs mainly at 500 K with a smaller state at 400 K.

TPD spectra after 0.84 L NO exposures on Pd films at 95 K are shown in fig. 7.9a - c for several Pd film thicknesses. These TPD spectra show the same general trends seen for 0.54 L NO exposures. The \( \theta_{pd} = 0.71 \) and the \( \theta_{pd} = 1.0 \) film have nearly identical TPD spectra with NO, N₂O and N₂ desorbing at 150 K and a second small N₂ desorption state at 350 K. As the Pd thickness increases, the low temperature desorption states for NO, N₂O and N₂ disappear. NO desorption occurs from a high temperature desorption state which resembles desorption from bulk Pd by \( \theta_{pd} = 3 \), but some differences exist in the low temperature desorption states seen on Pd(111) single crystals at this coverage. On the \( \theta_{pd} = 5 \) film, the two high temperature desorption states seen on Pd(111), \( \beta_2 \) and \( \beta_3 \), are observed. On the \( \theta_{pd} = 5 \) film, no N₂ desorption is observed, as on Pd(111).

TPD experiments following very large (224 L) NO exposures at 95 K were also performed as a function of Pd film thickness. These are shown in figs. 7.10a and 7.10b. Both NO desorption states \( \alpha_1 \) and \( \alpha_2 \) are seen at 130 and 160 K for a \( \theta_{pd} = 0.75 \) film in fig. 7.10a. NO TPD from the \( \theta_{pd} = 1.08 \) film shows no differences from that of the \( \theta_{pd} = 0.75 \) film. As the Pd film thickness increases to \( \theta_{pd} = 1.98 \), the NO desorption begins to broaden towards higher temperature and by \( \theta_{pd} = 3.02 \) new states are seen at 220 and 480 K. On the \( \theta_{pd} = 5 \) film NO desorption is identical to NO desorption from bulk Pd(111) single crystals with desorption states at 260, 295 and 490 K.
Figure 7.9 TPD Spectra following 0.84 L NO exposures at 95 K as a function of Pd film thickness.
(a) NO TPD spectra (30 amu), (b) N2O TPD spectra (44 amu), (c) N2 TPD spectra (28 amu).
Figure 7.10  TPD spectra following 224 L NO exposures at 95 K as a function of Pd film thickness. a) NO TPD spectra (30 amu), b) N$_2$O TPD spectra (44 amu).
Figure 7.10b shows the corresponding N2O TPD spectra. Similar to that observed for smaller NO exposures, the amount of N2O desorbing decreases, with no N2O desorbing from the $\theta_{Pd} = 5$ film, and no change in the desorption temperature as the film thickness increases. N2 TPD spectra are not very useful at this very large exposure. The amount of N2 desorbing remains nearly constant, decreasing only slightly as $\theta_{Pd}$ increases, indicating that a large portion of the N2 signal is due to the clean back and edges of the Ta(110) crystal. On all the Pd films studied, N2 desorption following 224 L NO exposures shows a broad desorption state at 160 K with a second, much smaller, desorption state seen at 360 K on the $\theta_{Pd} = 0.75$ film. This small peak shifts to higher temperature and decreases in intensity as the Pd film thickness increases.

Using the TPD areas we can monitor the amount of NO, N2O and N2 desorbing as the Pd film thickness increases. All three exposures (0.54, 0.84 and 224 L) show the same general trends and are presented in figs. 7.11a-c. The bcc(110) and fcc(111) monolayer Pd films show only a small amount of NO desorption. The amount of NO desorbing remains relatively constant until $\theta_{Pd} = 3$. At this point a large increase in the amount of NO desorbing is observed. A further increase in the amount of NO desorbing is seen for $\theta_{Pd} = 5$ films. If we compare the amount of NO desorbing from the $\theta_{Pd} = 1$ films and the $\theta_{Pd} = 5$ films for each of the three exposures we see that as the initial NO coverage is increased, the ratio of the NO TPD areas of the $\theta_{Pd} = 5$ to $\theta_{Pd} = 1$ film is decreased. Assuming that NO is reversibly adsorbed on the $\theta_{Pd} = 5$ film, we estimate that at low coverage, 14% of the NO is reversibly adsorbed on the Pd monolayer while 40% is reversibly adsorbed at saturation NO coverage. This implies that the fraction of NO decomposing on the Pd monolayer is inversely dependent on the initial NO coverage, i.e., a small initial NO coverage results in a large fraction of the NO being
Figure 7.11a  Comparison of the TPD areas of NO, N₂O and N₂ as a function of Pd film thickness for 0.54 L NO exposures.
Figure 7.11b Comparison of the TPD areas of NO, N$_2$O and N$_2$ as a function of Pd film thickness for 0.84 L NO exposures.
Figure 7.11c  Comparison of the TPD areas of NO, N$_2$O and N$_2$ as a function of Pd film thickness for 224 L NO exposures.
irreversibly adsorbed while a large initial NO coverage increases the propensity for reversible adsorption of NO. This type of behavior has also been observed for NO adsorbed on Rh(110) [19] and other surfaces and has been attributed to a reduction of the number of surface sites available for dissociation products.

The amount of N₂O desorbing from the bcc(110) and fcc(111) monolayer Pd films is slightly larger than the amount of NO desorbing for NO exposures of 0.54 and 0.84 L and is slightly smaller than the amount of NO desorbing for 224 L NO exposures. As the Pd film thickness increases the N₂O desorption yield gradually decreases with no N₂O desorbing from the θ_{pd} = 5 films. N₂ desorption is less sensitive to the Pd film thickness. The amount of N₂ desorbing gradually decreases as the Pd film thickness increases. However, the main contribution to N₂ desorption for these very large exposures is from the back and edges of the Ta(110) crystal as mentioned above.

### 7.3.3 NO Chemisorption on Unannealed Pd Films

TPD experiments following 0.54 L NO exposures at 95 K on unannealed Pd film deposited at 100 K on Ta(110) are shown in fig. 7.12a - c. On the θ_{pd} = 0.73, 1.06 and 1.98 films a very small amount of NO desorbs at 150 K (fig. 7.12a). On the θ_{pd} = 3.06 film NO desorption occurs at 500 K and the amount of NO desorbing has more than tripled when compared to the θ_{pd} = 1.06 film. Increasing the Pd film thickness to θ_{pd} = 5 causes a further increase in the amount of NO desorbing without changing the desorption temperature.

N₂O TPD spectra from unannealed Pd films following 0.54 L NO exposures are shown in fig. 7.12b. On the θ_{pd} = 0.73 film a very small amount of N₂O desorbs at 130 K. Increasing the Pd film thickness to θ_{pd} = 1.06 increases the amount of N₂O desorbing, but without a significant change in the desorption temperature. This is the first observation we have made of any difference in the
Figure 7.12 TPD spectra following 0.54 L NO exposures on unannealed Pd films at 95 K as a function of Pd film thickness. (a) NO TPD spectra (30 amu), (b) N$_2$O TPD spectra (44 amu), (c) N$_2$ TPD spectra (28 amu).
pseudomorphic and incommensurate monolayers. Further increases in the Pd film thickness do not change the desorption temperature but small changes in the amount of N$_2$O desorbing, with $\theta_{pd} = 1.98$ giving the largest N$_2$O yield, are observed. The corresponding N$_2$ TPD spectra are shown in fig 7.12c. On the $\theta_{pd} = 0.73$ film N$_2$ desorption states are observed at 115, 160 and 320 K. As the Pd film thickness increases to $\theta_{pd} = 1.06$ these desorption states broaden and become less defined while the amount of N$_2$ desorbing increases slightly. For a Pd thickness of $\theta_{pd} = 1.98$ the amount of N$_2$ desorbing increases further and the N$_2$ desorption state initially at 320 K on the $\theta_{pd} = 0.73$ film has now shifted up in temperature to 470 K.

Increasing the Pd film thickness to $\theta_{pd} = 3.06$ causes the low temperature state at 115 K to become much more prominent while the small state at 160 K has disappeared and the state at 470 K remains unchanged. The total amount of N$_2$ desorbing has increased further. On the $\theta_{pd} = 5$ film both desorption states at 115 K and 470 K have increased in size and another desorption state at 515 K has appeared.

TPD experiments were also conducted following saturation (224 L) NO exposures at 95 K on unannealed Pd films. These are shown in fig. 7.13a - c. On the $\theta_{pd} = 0.70$ film NO desorption occurs from a single state with a peak maximum of 140 K. This desorption state is much broader than the desorption state seen from an annealed Pd film of the same thickness for the same NO exposure. On the $\theta_{pd} = 1.03$ film the amount of NO desorption is nearly double that from the $\theta_{pd} = 0.70$ film. Increasing the Pd film thickness to $\theta_{pd} = 2.03$ causes a small increase in the amount of NO desorbing due to a new desorption state at 234 K. On the $\theta_{pd} = 3.07$ film this state has shifted up in temperature to 262 K and a third state is now seen at 480 K. At a Pd film thickness of $\theta_{pd} = 5$ the low temperature desorption state is at 150 K, the desorption state at 262 K on the $\theta_{pd} = 3.07$ film has shifted up to 294 K.
Figure 7.13 TPD spectra following 224 L NO exposures on unannealed Pd films at 95 K as a function of Pd film thickness.
(a) NO TPD spectra (30 amu), (b) N₂O TPD spectra (44 amu), (c) N₂ TPD spectra (28 amu).
and has developed a shoulder at 342 K, and the high temperature state has moved up to 490 K. The amount of NO desorbing is now more than twice that seen desorbing from the $\theta_{Pd} = 1.07$ film.

$N_2O$ desorption from the $\theta_{Pd} = 0.70$ film occurs from a single desorption state centered at 140 K (fig. 7.13b). This peak is much broader than the $N_2O$ desorption seen from an annealed Pd film. No change in the $N_2O$ TPD spectrum is observed on increasing the Pd film thickness to $\theta_{Pd} = 1.03$. For $\theta_{Pd} = 2.03$, the amount of $N_2O$ desorbing decreases by approximately one-half without a change in the desorption temperature. Increasing the Pd film thickness causes no changes in the $N_2O$ TPD spectra (the states seen at 290 K on the $\theta_{Pd} = 3.07$ and 5 films are due to a small amount of $CO_2$ desorption from the reaction of $CO_a + O_a$). The corresponding $N_2$ TPD spectra are shown in fig. 7.13c. For all of the unannealed Pd films studied, $N_2$ desorption is characterized by two desorption states. The first desorption state at 160 K is insensitive to Pd film thickness and neither the amount of $N_2$ desorbing from this state nor the desorption temperature are affected. The second state, initially at 365 K, shifts towards higher temperature with increasing film thickness ending up at 510 K on the $\theta_{Pd} = 5$ film. The $N_2$ TPD spectra observed after saturation NO exposures on the unannealed Pd films are very similar to $N_2$ desorption following saturation NO exposure on the annealed Pd films. This again points to a large contribution of the $N_2$ desorption signal being due to background effects since for these large exposures $N_2$ desorption appears to be independent of the Pd film thickness and preparation procedures.

Figures 7.14a and 7.14b show the TPD areas as a function of Pd film thickness for the unannealed films. For the 0.54 L exposures (fig. 7.14a) the amount of NO and $N_2O$ desorbing from the $\theta_{Pd} = 0.73$ and $\theta_{Pd} = 1.06$ films is small, approximately one fourth the amount which desorbs from annealed films of
Figure 7.14 Comparison of the TPD areas of NO, N$_2$O and N$_2$ as a function of Pd film thickness for unannealed Pd film. a) 0.54 L NO exposures, b) 224 L NO exposures.
the same thickness for the same NO exposure. The amount of N₂ desorbing from these unannealed Pd films is nearly the same as that desorbing from the annealed films. As the Pd film thickness increases, the amount of NO desorbing increases gradually. At a film thickness of \( \theta_{\text{Pd}} = 5 \) the amount of NO desorbing from the unannealed film is still one one fourth that desorbing from the annealed film. The amount of N₂O desorbing remains relatively constant as the Pd film thickness increases but drops off at \( \theta_{\text{Pd}} = 5 \). In contrast, the annealed Pd film shows no N₂O desorption. The amount of N₂ desorbing steadily increases as the Pd film thickness increases and on the \( \theta_{\text{Pd}} = 5 \) film is approximately 2.5 times the amount of N₂ desorbing from the annealed \( \theta_{\text{Pd}} = 5 \) film.

For 224 L exposures (fig. 7.14b) the amount of NO desorbing from the \( \theta_{\text{Pd}} = 0.70 \) and 1.03 unannealed films is nearly the same as that seen desorbing from annealed films of the same thickness. As \( \theta_{\text{Pd}} \) increases, the amount of NO desorbing increases and on the unannealed \( \theta_{\text{Pd}} = 5 \) film the amount of NO desorbing is slightly greater than that seen from the annealed \( \theta_{\text{Pd}} = 5 \) film. This is mainly due to the broadening of the desorption state corresponding to \( \beta_2 \) on Pd(111) single crystals. N₂O desorption following 224 L NO exposures on unannealed Pd films follows a similar trend as N₂O desorption from annealed Pd films gradually decreasing with increasing Pd film thickness. Similar to the 0.54 L NO exposures there is more N₂O desorbing from the unannealed \( \theta_{\text{Pd}} = 5 \) film than the annealed \( \theta_{\text{Pd}} = 5 \) film. As for other Pd films, N₂ desorption following 224 L NO exposures is complicated by a large contribution from the back and edges of the Ta crystal. Similar to the annealed Pd films, N₂ desorption is not sensitive to Pd film thickness for the unannealed films at these large exposures.
7.3.4 N₂O Chemisorption on Pd Films

A brief investigation of N₂O adsorption on Pd films was undertaken to further probe the reactivity of these Pd films and also to gain information about its formation from NO. Figure 7.15 shows TPD spectra following saturation N₂O exposures (224 L) on annealed θ₁₅ = 1 and θ₁₅ = 5 films at 95 K. On a θ₁₅ = 1 film N₂O desorbs from a low temperature state with a peak maximum at 115 K and a second broad state centered at 190 K. By performing experiments on clean Ta(110) the peak at 190 K was shown to be due to desorption from Ta(110). N₂O desorption from the θ₁₅ = 5 film is virtually identical to that seen from the θ₁₅ = 1 film with no change in the desorption temperatures or the TPD area. The low desorption temperature indicates that N₂O is weakly bound to both surfaces.

Figure 7.16 shows a series of HREELS spectra following a 224 L N₂O exposure on an annealed θ₁₅ = 1 film at 95 K and annealing to the specified temperature. At 95 K peaks are observed at 580, 1292, and 2236 cm⁻¹. These are assigned to the NNO bend, δ(NNO), the NO stretch, ν(NO) and the NN stretch, ν(NN) of molecularly adsorbed N₂O, respectively, in good agreement with those seen for gas phase N₂O as well as N₂O weakly adsorbed on other surfaces [20,21]. The peak at 2028 cm⁻¹ is due to CO adsorption from the background. Following an anneal to 110 K all the peaks attributed to N₂O have disappeared leaving the peak at 2076 cm⁻¹ and a broad peak centered at 964 cm⁻¹. Further annealing causes a reduction in the intensity of the broad peak at 964 cm⁻¹ and we tentatively assign this peak as due to adsorbed oxygen atoms.

Based on the TPD and HREELS experiments we propose that N₂O is initially adsorbed molecularly at 95 K. Upon heating the surface desorption and decomposition compete and cause the removal of N₂O from the surface.
Figure 7.15  $\text{N}_2\text{O}$ TPD spectra following 224 L $\text{N}_2\text{O}$ exposures to a $\theta_{\text{pd}} = 1$ and $\theta_{\text{pd}} = 5$ film at 95 K.
Figure 7.16 HREELS spectra following a 224 L N$_2$O exposure on a $\theta_{Pd} = 1$ film at 95 K and annealing to the specified temperature.
Figure 7.17 shows a direct comparison of N$_2$O desorption following a saturation N$_2$O exposure on a $\theta_{\text{Pd}} = 1$ film and N$_2$O desorption following saturation NO exposure on a $\theta_{\text{Pd}} = 1$ film. The rate-limiting step for N$_2$O desorption following NO exposures is not N$_2$O desorption, but rather NO decomposition or NO$_a$ + Na reaction. This is consistent with our NO HREELS results, which show no evidence of N$_2$O adsorbed on the Pd monolayer or thicker films following NO exposures. Based on the TPD areas, the amount of N$_2$O desorption following NO exposures on the $\theta_{\text{Pd}} = 1$ film is 18% of that observed following N$_2$O exposures on the $\theta_{\text{Pd}} = 1$ film.

### 7.4 Discussion

Our results using TPD and HREELS clearly show that NO chemisorption on ultrathin Pd films is much different from NO chemisorption on bulk Pd(111) single crystals. Adsorption of small amounts of NO on the Pd monolayer leads to population of both bridge and atop bonding sites. In contrast, on Pd(111) bridge sites are populated preferentially with atop sites being populated only at NO coverages $\theta_{\text{NO}} \geq 0.5$ [2]. Increasing $\theta_{\text{NO}}$ on the $\theta_{\text{Pd}} = 1$ film causes increased population of the atop sites resulting in an HREELS intensity ratio between bridge and atop sites of approximately 1:3. On Pd(111) the HREELS intensity ratio between bridge and atop sites is approximately 1:1. This indicates an increased propensity for population of atop sites on the $\theta_{\text{Pd}} = 1$ film relative to bulk Pd(111). For very large NO exposures a vibrational spectrum characteristic of N$_2$O$_3$ is observed. Formation of this species suggests that a low probability reaction is occurring for these high exposures.

Upon heating the surface, decomposition and desorption compete and cause the removal of NO from the surface. TPD experiments indicate that in addition to
Figure 7.17  Comparison of N$_2$O desorption following a 224 L NO exposure on a $\theta_{\text{Pd}} = 1$ film at 95 K and N$_2$O desorption following a 224 L N$_2$O exposure on a $\theta_{\text{Pd}} = 1$ film at 95 K.
NO, N₂O and N₂ are formed and desorb. HREELS experiments indicate N₂O and N₂ are formed only during the heating of the crystal and desorb as soon as they are formed. Analysis of the TPD spectra of these species shows that all are bound to the surface weakly and desorb with activation energies of less than 10 kcal/mol. These results also show that the Pd monolayer is very different from Pd(111) surfaces where the NO-Pd bond strength is 38 kcal/mol at low θ_{NO} and adsorption is completely reversible. We can also compare the chemistry of the θ_{Pd} = 1 film to a stepped Pd(111) surface. Schmick et al. studied NO adsorption on a stepped Pd(111) surface inclined 3° to the (111) face [22]. They observed decomposition of NO and the desorption products included NO, N₂O and N₂. However, N₂O and N₂ desorbed at temperatures above 400 K and were attributed to decomposition of NO on step sites. Thus, we can rule out the altered chemisorption properties of the θ_{Pd} = 1 film being mainly due to surface roughness or defects in the Pd film. Decomposition of NO has also been observed on Rh(111) [23] and Ag(111) surfaces [24,25]. In the case of Rh(111), desorption of NO, O₂ and N₂ were observed at temperatures above 400 K. No N₂O desorption was observed. In contrast, on Ag(111) NO, N₂O and N₂ were found to desorb below 200 K while O₂ was seen to desorb at a temperature of 510 K. Because of the similarities of NO desorption from a Ag(111) surface and the θ_{Pd} = 1 film a more detailed discussion and comparison of the two surfaces is warranted.

At low NO exposures on a Ag(111) surface, a single desorption peak of NO was seen at about 100 K [24,25]. The peak desorption temperature shifts upward by 13 K with increasing NO exposure. At higher exposure, a new NO desorption state was observed at 90 K with much smaller desorption states at 190 and 400 K. The desorption temperature of the state at 90 K did not change with increasing exposure. At saturation coverage, N₂O was seen to desorb at the same temperature
as the low temperature NO peaks (90 and 113 K). However, for NO, the peak height ratio of the desorption state at 90 K to the desorption state at 113 K was 5.0 while for N$_2$O this ratio was only 0.47. The desorption of N$_2$ at these temperatures was attributed to cracking of N$_2$O in the mass spectrometer.

This is quite similar to the desorption features observed on the $\theta_{pd} = 1$ film shown in figs. 7.1a - c and discussed in section 3.1.1. Both surfaces initially show a single, low temperature NO desorption state which shifts up in temperature as the coverage is increased. Further NO exposure causes a second NO desorption state to be populated with a constant desorption temperature below that of the first state on both surfaces. There is also much less N$_2$O desorption seen for the low temperature N$_2$O desorption state relative to the higher temperature N$_2$O state on both surfaces. However, we do observe N$_2$ desorption which cannot be accounted for by the cracking fraction of N$_2$O, we do not observe the 190 or 400 K NO desorption states and no O$_2$ desorption was ever detected.

**Table II: Vibrational Frequencies for NO/Ag(111)**

<table>
<thead>
<tr>
<th>Mode</th>
<th>Small NO Exposure</th>
<th>Saturation NO Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-NO</td>
<td>234</td>
<td>250</td>
</tr>
<tr>
<td>NO bend of N$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>not assigned</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_2$ NO bend</td>
<td>846</td>
<td></td>
</tr>
<tr>
<td>$A_2$ NO stretch</td>
<td>1153</td>
<td>1153</td>
</tr>
<tr>
<td>$A_1$ NO stretch</td>
<td>1282</td>
<td>1274</td>
</tr>
<tr>
<td>$t_2$ NO stretch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_1$ NO stretch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NN stretch of N$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2258</td>
<td></td>
</tr>
</tbody>
</table>
In addition to TPD experiments, we can compare HREELS data for the NO/Ag(111) system [25] with our results on the θ_{Pd} = 1 film. Table II lists the observed vibrational losses and their assignments for small and saturation NO exposures at 80 K for Ag(111). In table II, Δ₁ refers to a linear NO species adsorbed in a three-fold bridge site, Δ₂ refers to a bent or tilted NO species adsorbed in a three-fold bridge site, t₁ refers to linear NO adsorbed at an atop site, and t₂ refers to bent NO adsorbed at an atop site. For small NO exposures on Ag(111) the loss peaks have been interpreted as being due to linear and bent threefold bridge bonded NO species and coadsorbed N atoms. Thus NO is adsorbed both dissociatively and molecularly at 80 K. Compared to small NO exposures on the θ_{Pd} = 1 film, the loss peaks observed on Ag(111) are quite different since NO is adsorbed molecularly on the θ_{Pd} = 1 film also. At saturation NO exposure the observed peaks are attributed to a combination of various NO species (bridge bonded - bent, bridge bonded - linear, atop - bent, atop - linear) coadsorbed with N₂O. However, it is worth pointing out that many of the peaks agree quite well with those attributed to an N₂O₃ species on Au(111) and N₂O₃ on the θ_{Pd} = 1 film (see Table I). Thus it is possible that NO, N₂O and N₂O₃ are all coadsorbed on the Ag(111) surface at 80 K. In contrast, no evidence of a stable N₂O species was seen for the θ_{Pd} = 1 film.

Because the adsorption of NO on many surfaces is similar to adsorption of CO it is interesting to compare their adsorption on a θ_{Pd} = 1 film. While a substantial amount of NO dissociates during TPD experiments, adsorption of CO is completely reversible. Analysis of TPD spectra of CO on θ_{Pd} = 1 films on many refractory metal substrates shows that in all cases the CO-Pd bond strength is 20 kcal/mol or less, a large reduction from that observed on Pd(111) or Pd(100) surfaces. LEED observations of CO adsorption on a θ_{Pd} = 1 film on Ta(110)
indicate that CO can reverse the phase transition from bcc(110) to fcc(111) at high enough $\theta_{\text{CO}}$ leaving a bcc(110) Pd monolayer. NO adsorption, on the other hand, removes all spots from the LEED pattern indicating complete disorder. Similar to NO, CO adsorption on a $\theta_{\text{Pd}} = 1$ film also shows an increased propensity for population of atop sites relative to the bulk Pd surface.

While the $\theta_{\text{Pd}} = 1$ film shows only low temperature desorption of NO, N$_2$, and N$_2$, the trend for NO chemisorption as a function of Pd film thickness is towards bulk Pd(111) characteristics. The change is not gradual. The $\theta_{\text{Pd}} = 2$ film closely resembles the $\theta_{\text{Pd}} = 1$ film with the most significant difference being a decrease in the amount of NO, N$_2$O and N$_2$ desorbing. A large change occurs for a Pd film thickness of $\theta_{\text{Pd}} = 3$. At this Pd thickness the propensity for reversible NO adsorption increases dramatically due to the population of higher temperature NO desorption states which resemble desorption states on Pd(111) single crystals. Also at this thickness there is still a significant population of low temperature NO desorption states as well as low temperature N$_2$O and N$_2$ desorption. This indicates that the Pd films are not flat and a range of thicknesses exists for these Pd films. By $\theta_{\text{Pd}} = 5$ the properties of the surface resemble bulk Pd(111) surfaces with respect to NO chemisorption.

For unannealed Pd films we simply see the expected effects of surface roughness. When $\theta_{\text{Pd}} \leq 1$ the amount of NO desorbing is less than what is seen on the annealed Pd film while for thicker Pd films the amount of NO desorbing is actually increased slightly due to a slightly increased surface area. In contrast to the annealed Pd film N$_2$O is seen to desorb even from the $\theta_{\text{Pd}} = 5$ films. This is consistent with an increased surface roughness which implies a greater number of surface imperfections.
7.5 Summary

We have studied the NO chemisorption properties of monolayer and ultrathin Pd films deposited on Ta(110). Our investigations show that NO adsorption is molecular on the Pd monolayer film at 95 K. Temperature programed desorption (TPD) experiments show NO, N$_2$O and N$_2$ desorption products. High resolution electron energy loss spectroscopy (HREELS) is used to determine that N$_2$O and N$_2$ are not adsorbed on the surface but are formed only during the TPD experiment. In addition, it is found that N$_2$O$_3$ is formed on the Pd monolayer film. NO chemisorption is a sensitive chemical probe of the electronic structure and reactivity of Pd metal films. We find that in many respects the interaction of NO with the Pd monolayer film resembles that of a Ag(111) surface, consistent with our suggestion, and that of others, that charge transfer or Pd s-d rehybridization fills the Pd d-band, producing a Pd surface with the reactivity of Ag. As the Pd film thickness is increased the surface reactivity begins to resemble bulk Pd(111) surfaces, with some "tuning" of the NO chemisorption properties for Pd films in the thickness range of 2 - 3 layers. N$_2$O is weakly bound to the Pd films and desorbs by 115 K. This indicates that N$_2$O desorption seen following NO exposures is reaction rate limited.
REFERENCES FOR CHAPTER VII

[18] A. Sellidj and B. E. Koel, to be submitted
CHAPTER VIII

HYDROGEN ADSORPTION AND ABSORPTION ON ULTRATHIN Pd FILMS ON Ta(110)

8.1 Introduction

Interactions of hydrogen with metal surfaces are important for critical technologies and aid in a fundamental understanding of chemical reactions at surfaces [1]. Hydrogen plays an immensely important role in the chemistry of heterogeneous catalysis where many reactions involve hydrogen as reactant, intermediate, or product. Penetration of hydrogen atoms into the bulk of metals is important for hydrogen storage and hydrogen-induced embrittlement of metals. From a fundamental point of view, dissociative chemisorption of hydrogen on metal surfaces is one of the most simple heterogeneous chemical reactions.

Our interest was drawn by work by Strongin and coworkers involving monolayer and ultrathin Pd films deposited on Nb and Ta recrystallized foils [2-5]. Using bulk resistivity measurements, they found that Pd film coverages less than or equal to one pseudomorphic Pd monolayer caused no change in the hydrogen uptake or slightly inhibited hydrogen uptake compared to hydrogen absorption into clean Nb and Ta. At Pd coverages slightly greater than one monolayer they observed a phase transition from a pseudomorphic Pd monolayer to an incommensurate fcc (111) structure. After this phase change occurred an increased hydrogen uptake rate was observed. They proposed that the increased uptake was a direct consequence of the difference in the number of nearest neighbors between the two Pd structures and the different electronic structures in the two cases. The rate of hydrogen uptake
increased further with Pd film thickness and reached a maximum value at a Pd thickness of about 5 layers. The hydrogen uptake rate remained at this maximum value for Pd films up to 100 layers thick. The sticking coefficient for hydrogen was estimated to be unity for these thicker films. They concluded that by combining the surface properties of Pd with the bulk properties of Nb or Ta, the barrier for hydrogen migration into the bulk was reduced and this lead to an order of magnitude increase in the solution rate.

The Pd hydrogen system is a classic metal hydrogen system and it has received a great deal of attention [6,7]. Small H$_2$ exposures on Pd(111) at room temperature produce a single H$_2$ TPD peak at 370 K [8,9]. A second desorption state is observed near 673 K upon increasing the exposure. These peaks are attributed to chemisorbed hydrogen (β state) and hydrogen which was originally absorbed in the bulk, respectively. Stulen and coworkers [10, 11] have extended the H$_2$ TPD experiments to include exposure temperatures as low as 5 K. An H$_2$ multilayer desorbs by 9 K leaving a molecular H$_2$ species adsorbed on the surface. Desorption of this species occurs at 16 K and was denoted as the Γ-H$_2$ desorption state [10]. The dissociative chemisorption state (β state) desorbs at 300 K. For H$_2$ exposures at 80 K, only desorption from the β state was observed [9]. However, for exposure temperatures between 90 and 140 K a new desorption peak, designated as α, appeared with a desorption temperature of 170 K. The α state did not saturate with increasing H$_2$ exposure and exhibited zero order desorption kinetics. This state was attributed to absorption into Pd to populate a near surface hydride state. Population of the α state was found to be thermally activated with a maximum population rate at an exposure temperature of 115 K. It was also shown that roughening the surface by Ar$^+$ ion bombardment enhances the rate of population of
the $\alpha$ state by up to a factor of 4 at 115 K, suggesting that surface defects are important in the absorption kinetics [9].

TPD studies of H$_2$ adsorbed on the Pd(100) and Pd(110) surfaces show that the desorption temperature of chemisorbed hydrogen is only slightly different on these crystal faces [12,13]. An interesting effect is seen on Pd(110) where two subsurface hydrogen states, denoted as $\alpha_1$ and $\alpha_2$, are populated and desorb at 160 and 225 K respectively [13].

In this chapter H$_2$ adsorption and absorption studies on ultrathin Pd films on a Ta(110) single crystal substrate are discussed. TPD was used since it is much more sensitive to the hydrogen coverage and the type of hydrogen adsorbed than bulk resistivity measurements. We show that the hydrogen chemisorption state is destabilized on the $\theta_{Pd} = 1$ film relative to bulk Pd(111) surfaces and that it is only populated in substantial amounts for $\theta_{Pd} > 3$ layers. The sticking coefficient is also reduced on the $\theta_{Pd} = 1$ film relative to bulk Pd(111) surfaces. Additionally, we investigate the importance of the Pd film preparation procedure which were not discussed in the previous work. The $\alpha$ state is clearly observed for $\theta_{Pd} \geq 1$ and the population of this state is highly dependent on the Pd film preparation procedures.

8.2 Experimental Information

The experimental apparatus has been described in chapter II. The heating rate during TPD experiments was 5 K/sec. All Pd coverages are referenced to the fcc (111) Pd monolayer, with $\theta_{Pd} = 1$ corresponding to a Pd coverage equal to the Pd(111) surface atom density [14]. H$_2$ exposures were carried out with the aid of a glass capillary array doser resulting in a small flux enhancement. Exposures are reported in units of Langmuir (1 L = 1 x 10-6 torr-s) and have been corrected for ionization gauge efficiency and doser enhancement factor.
Hydrogen penetration into the bulk of Ta occurs even for temperatures as low as 78 K [15]. Thus, the surface of the Ta(110) crystal will not become saturated under our experimental conditions. In order to estimate the amount of $H_2$ desorbing during $H_2$ TPD experiments, we made comparisons to CO TPD spectra from thick Pd films after making corrections for ionization efficiency and mass spectrometer transmission differences for the two molecules. In our studies, approximately one monolayer of hydrogen desorbs from clean Ta(110) following a 4.6 L $H_2$ exposure at 100 K.

The growth and structure of Pd films on Ta(110) have been studied[4,14,16,17]. At room temperature, the growth is best described by a Frank-van der Merwe (layer-by-layer) growth mechanism. Initially, the first Pd layer grows in two dimensional pseudomorphic islands. This continues up to $\theta_{Pd} = 0.65$, with near completion of the Pd bcc(110) monolayer. Subsequent deposition of Pd causes a structural phase transition to occur, forming Pd fcc(111) islands. This transition causes "beat" spots aligned parallel to the short axis of the distorted hexagon of the substrate to appear in the LEED pattern. For $\theta_{Pd} = 1.0$ an fcc(111) Pd monolayer is formed with a surface atom density approximately equal to that of bulk Pd(111). As further Pd is deposited, the film continues to grow with an fcc(111) structure. The beat pattern observed in LEED fades and a symmetric hexagon characteristic of the fcc(111) structure is observed. The growth of Pd on Ta(110) at 125 K is similar to that at 300 K although the growth deviates slightly from the layer-by-layer mode. Through annealing experiments it was shown that the bcc(110) pseudomorphic Pd monolayer is stable to 1350 K, but the fcc(111) monolayer is stable only to 550 K. Near this temperature, the beat pattern begins to fade and streaking is observed. Films thicker than this may agglomerate into three dimensional clusters two to three layers thick at temperatures as low as 370 K.
8.3 Results

The H$_2$ TPD spectra obtained subsequent to H$_2$ exposures to a clean Ta(110) surface at 100 K are shown in fig 8.1. The majority of H$_2$ desorption occurs in the region 800 - 1600 K after small H$_2$ exposures (0.09 L). With increasing exposure, the state at 1100 K increases in size, becoming extremely broad, and gradually shifts to about 1000 K. This H$_2$ desorption feature is not saturated by a 22 L H$_2$ exposure at 100 K and desorbs over an 800 degree temperature range. The behavior of this peak with increasing H$_2$ exposures suggests that it is due to desorption of hydrogen which is absorbed in the bulk of the Ta(110) crystal. A small amount of H$_2$ desorption is also seen at 150, 385, and 615 K. The H$_2$ TPD from Ta(110) is in good agreement with previous work [17].

8.3.1 The Interaction of H$_2$ with the Incommensurate fcc(111) Monolayer Pd Film, $\theta_{Pd} = 1$

Studies of H$_2$ adsorption on $\theta_{Pd} = 1$ films deposited on the Ta(110) surface at 100 K were carried out. The Pd films were not annealed prior to exposure to H$_2$ and clearly showed the "beat" pattern in LEED observations. Figure 8.2 shows H$_2$ TPD spectra for increasing H$_2$ exposures at 100 K. Two spectra from clean Ta(110) are also shown by dashed curves for comparison. For a small H$_2$ exposure of 0.09 L, a new H$_2$ TPD peak is observed at 1400 K and the TPD state at 150 K is clearly enhanced relative to the clean Ta(110) surface. Approximately twice as much H$_2$ desorbs at this temperature following deposition of the $\theta_{Pd} = 1$ film. However, the overall shape of the H$_2$ TPD spectrum appears to be largely unaffected by deposition of the $\theta_{Pd} = 1$ film.

As the H$_2$ exposure is increased, the peak at 1100 K increases in size and shifts to lower temperature in a similar fashion as observed on clean Ta(110). Slightly less H$_2$ desorbs from this state for $\theta_{Pd} = 1$ compared to clean Ta(110) for
Figure 8.1  H$_2$ TPD spectra as a function of H$_2$ exposure at 100 K from clean Ta(110).
Figure 8.2 $H_2$ TPD spectra as a function of $H_2$ exposure at 100 K from a one monolayer Pd film deposited on Ta(110).
equivalent H\textsubscript{2} exposures. The desorption state at 1400 K retains a constant size and desorption temperature as the H\textsubscript{2} exposure is increased while a slight increase in the amount of H\textsubscript{2} desorption from the state at 150 K is observed. For the 22 L H\textsubscript{2} exposure a small shoulder is observed on the high temperature side of the 150 K desorption state.

A comparison of the total H\textsubscript{2} TPD area as a function of H\textsubscript{2} exposure for clean Ta(110) and the \( \theta_{\text{Pd}} = 1 \) film is shown in fig. 8.3. As discussed above, the

![Graph](image)

Figure 8.3  H\textsubscript{2} TPD area as a function of H\textsubscript{2} exposure at 100 K for the data of figs. 8.1 and 8.2.
total H$_2$ TPD area increases with H$_2$ exposure due mainly to an increased population of the state at 1100 K. For small H$_2$ exposures the amount of H$_2$ desorbing from clean Ta(110) and the $\theta_{pd} = 1$ film are nearly the same. However, for larger exposures slightly more hydrogen desorbs from clean Ta(110). From fig. 8.3 we can obtain the sticking coefficient as a function of H$_2$ exposure since the slope of the TPD area vs. exposure plot is proportional to the sticking coefficient. The values of S were normalized by comparison to H$_2$ exposures on clean Ta(110) at 300 K and assuming that at this temperature S = 0.05 which is the value determined on recrystalized Ta foils [3]. For small H$_2$ exposures S is 0.41 for clean Ta(110) and 0.58 for the $\theta_{pd} = 1$ film. These high values are likely due to defect sites which are known to play an important role in the sticking coefficient of H$_2$ on metal surfaces [1]. The value of S rapidly decreases with increasing H$_2$ exposure and reaches a value of 0.04 for both clean Ta(110) and the $\theta_{pd} = 1$ film by an H$_2$ exposure of 4.6 L. The value of S remains constant as the H$_2$ exposure is increased further indicating that at this exposure temperature and coverage regime, S is dominated by diffusion into the bulk of the sample.

Several interesting observations about H$_2$ desorption from the $\theta_{pd} = 1$ film can be made. First, the desorption state at 150 K on the $\theta_{pd} = 1$ film is at the temperature at which the $\alpha$ state due to H$_2$ desorption from decomposition of a Pd hydride is observed for bulk Pd(111) surfaces. This indicates that we have populated this state for the $\theta_{pd} = 1$ film. Second, there is only a very slight increase in the desorption features between 200 and 400 K relative to clean Ta(110) after deposition of a $\theta_{pd} = 1$ film and only for a large (22 L) H$_2$ exposure. This is where we would expect to observe desorption due to hydrogen chemisorbed on Pd. That there is no distinct peak in this temperature range above what is seen on clean Ta(110) suggests that there is no substantial amount of hydrogen actually
chemisorbed on the surface of the $\theta_{Pd} = 1$ film. Finally, because absorption occurs for Ta even at 78 K [15] the observed value of $S$ will be a function of the adsorption coefficient, $S_{ads}$, and the absorption coefficient, $S_{sol}$. At 100 K the rate of hydrogen diffusion into the Ta bulk, and thus $S_{sol}$, will be small [6,15]. Thus, for $H_2$ exposures at 100 K the value of $S$ at low hydrogen exposures appears to be dominated by surface defects while at higher $H_2$ exposures absorption into the bulk is rate limiting.

LEED observations were performed as a function of $H_2$ exposure at 100 K. A $\theta_{Pd} = 1$ film was deposited at 100 K and then annealed to 300 K to improve the quality of the LEED pattern. As discussed in the experimental section, at this Pd film thickness beat spots are observed which are aligned parallel to the short axis of the distorted hexagon of Ta(110). Exposure of $H_2$ to this surface causes no change (including no increase in the background intensity) in the LEED pattern for $H_2$ exposures as high as 22 L. This is consistent with there being very little hydrogen adsorbed on the $\theta_{Pd} = 1$ film.

8.3.2 The Interaction of $H_2$ with Pd Films of Increasing Thickness

$H_2$ TPD spectra following 4.6 L $H_2$ exposures at 100 K are shown in fig. 8.4 for several Pd film thickness. These Pd films were deposited on Ta(110) at 100 K and were not annealed prior to exposure to $H_2$. The $H_2$ TPD from clean Ta(110) is also shown for comparison as the dashed curve in fig. 8.4. Results for the pseudomorphic bcc(110) $\theta_{Pd} = 0.71$ film are almost identical to the fcc(111) $\theta_{Pd} = 1$ film, with the peak at 1000 K broadened towards higher temperature due to population of the desorption state at 1400 K. A small decrease in the amount of $H_2$ desorbing compared to clean Ta(110) and the $\theta_{Pd} = 1$ film is observed. Another small difference from the $\theta_{Pd} = 1$ film is that there is no discernable increase in $H_2$ desorption at 150 K. One brief report of hydrogen adsorption on a thin Pd film
Figure 8.4  \( \text{H}_2 \) TPD as a function of Pd film thickness following 4.6 L \( \text{H}_2 \) exposures at 100 K.
deposited on Ta(110) studied by TPD has shown a similar result for this Pd film thickness [17]. Increasing the Pd film thickness to \( \theta_{\text{Pd}} = 2 \) causes a substantial increase in the size of the desorption state at 150 K (\( \alpha \) state) as well as the desorption state at 1000 K, with an increase in the total amount of \( \text{H}_2 \) desorbing. There is also a small shoulder on the high temperature side of the \( \alpha \) state at 250 K. At a Pd film thickness of \( \theta_{\text{Pd}} = 3.5 \), the amount of \( \text{H}_2 \) desorbing from the \( \alpha \) state has more than doubled relative to the \( \theta_{\text{Pd}} = 2 \) film and the total amount of \( \text{H}_2 \) desorption has also increased. The shoulder on the high temperature side of the \( \alpha \) state has now become a very small peak at 312 K and is attributed to desorption of hydrogen chemisorbed on Pd(111) sites (\( \beta \) state). For \( \theta_{\text{Pd}} = 15 \), the \( \alpha \) state has further increased in size, the \( \beta \) state has increased in size and shifted up to 324 K, and the peak due to desorption from bulk Ta has increased in size and shifted down to 900 K. Increasing the Pd film thickness to \( \theta_{\text{Pd}} = 50 \) causes large increases in the \( \alpha \) state, chemisorbed hydrogen state and the high temperature desorption state due to desorption from bulk Ta. In addition, a new state appears at 1640 K. Relative to the \( \theta_{\text{Pd}} = 1 \) film this is more than a five fold increase in the total amount of \( \text{H}_2 \) desorbing.

Some experiments were also carried out 500 K in order to compare with the previous work of Strongin and coworkers [2-5]. \( \text{H}_2 \) TPD spectra following 4.6 L \( \text{H}_2 \) exposures on several Pd films on Ta(110) at 500 K are shown in fig. 8.5. All of the Pd films were annealed to 500 K prior to \( \text{H}_2 \) exposure to minimize structural changes during the exposure and subsequent TPD experiments. A new Pd film was deposited for each exposure and TPD experiment conducted, and the samples were cooled to 100 K just prior to TPD. The \( \text{H}_2 \) TPD from clean Ta(110) is shown by the dashed curve in fig. 8.5. Two peaks are seen at 980 and 1535 K. Upon deposition of a \( \theta_{\text{Pd}} = 0.8 \) film the peak at 980 K is decreased in size
Figure 8.5  \( \text{H}_2 \) TPD as a function of Pd film thickness following 4.6 L \( \text{H}_2 \) exposures at 500 K.
and is broadened towards higher temperature due to population of the state at 1400 K. LEED observations showed that the Pd adlayer is pseudomorphic with the Ta(110) substrate at this Pd coverage. Increasing the Pd coverage to $\theta_{pd} = 1.0$ causes a small increase in the amount of H$_2$ desorbing. At a Pd film thickness of $\theta_{pd} = 2.0$ the amount of H$_2$ desorbing nearly doubles relative to the $\theta_{pd} = 1$ film. A similar increase in the amount of H$_2$ desorbing is seen after increasing the Pd film thickness to $\theta_{pd} = 3$. For a $\theta_{pd} = 5$ film the amount of H$_2$ desorbing increases still further and the peak maximum has shifted down to about 850 K. Increasing the Pd film thickness to $\theta_{pd} = 10$ results in only a small increase in the amount of H$_2$ desorbing.

Figure 8.6 shows the H$_2$ TPD area plotted as a function of the Pd film thickness for 4.6 L H$_2$ exposures at 100 and 500 K. The H$_2$ TPD area initially decreases as Pd is deposited for both exposure temperatures. The TPD area then increases slightly for a Pd film thickness of $\theta_{pd} = 1$. For exposures at 100 K, a gradual increase is observed as the Pd film thickness increases. This increasing trend continues even for films as thick as $\theta_{pd} \approx 50$. For H$_2$ exposures at 500 K the H$_2$ TPD area increases rapidly for $1 \leq \theta_{pd} \leq 3$, and reaches a constant value at $\theta_{pd} = 5$.

Because equal amounts of H$_2$ were exposed to each of the Pd films the TPD area measures the relative H$_2$ sticking coefficient, S. This shows that on clean Ta(110) and all the Pd films S is much higher for H$_2$ exposures at 500 K relative to H$_2$ exposures at 100 K. At 500 K absorption into Ta is fast [6,18] and therefore the uptake rate should be limited by adsorption rather than absorption. This implies that the value of S will be representative of $S_{ads}$. By normalizing the data to an uptake on clean Ta(110) at 300 K where $S = 0.05$ [3] we can determine the sticking coefficient of the other Pd films and clean Ta(110). Based on this we determine that
Figure 8.6  H$_2$ TPD area as a function of Pd film thickness for 4.6 L H$_2$ exposures at 100 K and 500 K. Also shown by the right hand axis are the relative values of the sticking coefficient.
$S_{ads}$ for clean Ta(110) is 0.10 at 500 K. The value of $S_{ads}$ for the pseudomorphic Pd monolayer is 0.09 at 500 K while for the fcc(111) Pd monolayer $S_{ads} = 0.11$ at 500 K. For the $\theta_{Pd} = 10$ film $S = 0.43$ which is close to the value of 0.5 determined for bulk Pd(111) at 80 K [1].

For an exposure temperature of 100 K the value of $S$ will be a function of $S_{ads}$ and $S_{sol}$ as discussed above. Thus, we can not distinguish between $S_{ads}$ and $S_{sol}$ at this temperature. By comparing the data taken at 100 K to the H$_2$ uptake on clean Ta(110) at 300 K we can obtain values of $S$ for H$_2$ for the 100 K exposures. This gives $S = 0.04$ for clean Ta(110), $S = 0.03$ for the pseudomorphic Pd monolayer, and $S = 0.04$ for the fcc(111) Pd monolayer at 100 K.

LEED observations of the $\theta_{Pd} = 10$ film showed a symmetric hexagonal pattern indicative of a Pd fcc(111) structure after annealing to 300 K. Similar to the $\theta_{Pd} = 1$ film, no changes were observed in the LEED pattern for H$_2$ exposures as large as 22 L.

**8.3.3 The Structure and Chemical Properties of Annealed Pd Films as Probed by H$_2$ Adsorption/Desorption**

Surface roughness has been shown to be important to the rate of population of the $\alpha$ state [9]. In light of this, we have attempted to use H$_2$ desorption from the $\alpha$ state to study the Pd film morphology and properties as a function of annealing temperature, $T_{ann}$. Figure 8.7 shows the H$_2$ TPD spectra following 4.6 L H$_2$ exposures to $\theta_{Pd} = 3$ films at 100 K, systematically increasing the annealing temperature (prior to H$_2$ exposure). Larger H$_2$ exposures were used for some ($T_{ann} = 100$ K) of the $\theta_{Pd} = 3$ films, but this did not cause an increase in the amount of desorption from the $\alpha$ state. This indicates that a 4.6 L H$_2$ exposure is sufficient to saturate the $\alpha$ state at this film thickness. For an unannealed $\theta_{Pd} = 3$ film ($T_{ann} = 100$ K) there is a large amount of H$_2$ desorbing from the $\alpha$ state. As the annealing...
Figure 8.7  H₂ TPD spectra from a θ_{Pd} = 3 film following 4.6 L H₂ exposures at 100 K as a function of preannealing temperature.
temperature is increased the amount of H\(_2\) desorbing from the \(\alpha\) state decreases and by an annealing temperature of 400 K the \(\alpha\) state is no longer populated. The absence of desorption from the \(\alpha\) state continues between 400 and 600 K. At an annealing temperature of 700 K, H\(_2\) desorption from the \(\alpha\) state is again visible. The \(\alpha\) state increases in size for an annealing temperature of 800 K and then decreases again as the annealing temperature is increased. No desorption from the \(\alpha\) state is observed by an annealing temperature of 1100 K. This exact same trend was observed with a Pd film thickness of \(\theta_{\text{Pd}} = 2\). The only differences were a smaller amount of desorption from the \(\alpha\) state and no desorption from the \(\alpha\) state by an annealing temperature of 1000 K rather than 1100 K as with the \(\theta_{\text{Pd}} = 3\) films.

Figure 8.8a shows the TPD area of the \(\alpha\) state plotted against annealing temperature of the \(\theta_{\text{Pd}} = 3\) films. This clearly shows the decrease in the TPD area of the \(\alpha\) state as the Pd film is annealed to 400 K, the plateau between 400 and 600 K where no H\(_2\) desorption from the \(\alpha\) state occurs, the increase from 600 to 800 K, and the second decrease to 1100 K where no H\(_2\) desorption from the \(\alpha\) state occurs. Figure 8.8b shows the total H\(_2\) TPD area as a function of the annealing temperature. There is a gradual increase in the total TPD area as the annealing temperature is increased to 600 K and then a decrease as the annealing temperature approaches 1100 K.

To determine what effect, if any, surface roughness and defects play, we carried out some experiments using Ar\(^+\) ion sputtering. We compared H\(_2\) desorption from an unannealed \(\theta_{\text{Pd}} = 3\) film, a \(\theta_{\text{Pd}} = 3\) which had been annealed to 400 K, and a \(\theta_{\text{Pd}} = 3.5\) film which was annealed to 400 K then briefly sputtered with 0.5 kV Ar\(^+\) ions to a thickness of \(\theta_{\text{Pd}} \approx 3\). Figure 8.9 shows the H\(_2\) TPD spectra from these Pd films following 4.6 L H\(_2\) exposures at 100 K. The unannealed \(\theta_{\text{Pd}} = 3\) film shows desorption from the \(\alpha\) state at 150 K and the \(\theta_{\text{Pd}} = 3\)
Figure 8.8  \( \text{H}_2 \) TPD area as a function of preannealing temperature. (a) TPD area of the \( \alpha \) state. (b) Total TPD area.
Figure 8.9  Comparison of unannealed, annealed, and sputtered Pd films.
film annealed to 400 K shows no H₂ desorption from the α state. The θ_{pd} = 3.5 film annealed to 400 K but then sputtered to θ_{pd} = 3 shows H₂ desorption from the α state. This is a clear indication that the effect we observe on the Pd films is a result of the same processes that are involved on bulk Pd(111).

8.4 Discussion

The H₂ adsorption and absorption properties of Pd are significantly modified by forming ultrathin films on Ta(110). The sticking coefficient, S, for H₂ on the θ_{pd} = 1 film at 100 and 500 K is clearly much lower than it is for thick Pd films or bulk Pd(111) surfaces but is close to the value of S for Ta(110). At 100 K, S is a function of both S_{ads} and S_{sol}. Because a diffusion barrier must be overcome for penetration into the bulk this limits the uptake rate at 100 K. At 500 K diffusion into the bulk is rapid, but S is small due to a low value of S_{ads}.

In addition to the small value of S_{ads} for H₂ on the θ_{pd} = 1 film, no significant population of a chemisorption state is observed at this film thickness. This is consistent with electron stimulated desorption results which point to the absence of atomic hydrogen on the surface [5]. This is a stark contrast to bulk Pd(111) surfaces where the chemisorption state is preferentially filled. We propose that this is due to a destabilization of this state and an activation barrier to dissociative adsorption caused by extensive bonding interactions between Pd and Ta. Figure 8.10 shows a potential energy diagram for H₂ interacting with a bulk Pd(111) surface. A gas phase H₂ molecule impinging on the surface will first encounter the physisorption well of depth E_{H₂}. The H₂ molecule will either be scattered back into the gas phase or will cross over into the chemisorption well. Since there is no evidence for an activation barrier for H₂ adsorption on bulk Pd(111) [19] the intersection of these two curves lies below the zero of potential energy. Once the chemisorption sites on Pd(111) are saturated hydrogen may begin
Figure 8.10  Comparison of potential energy diagrams for the interaction of hydrogen with a surface. The thin line represents the interaction with bulk Pd while the thick line represents interaction with a $\theta_{Pd} = 1$ film deposited on Ta(110).
to populate the $\alpha$ state. Population of the $\alpha$ state has been shown to be thermally activated and so a small barrier must be overcome to populate these sites [9]. An additional diffusion barrier must then be overcome to populate bulk absorption sites. Figure 8.10 also shows the corresponding potential energy diagram for a $\theta_{\text{Pd}} = 1$ film deposited on Ta(110). The small sticking coefficient of H$_2$ on the $\theta_{\text{Pd}} = 1$ films could be due to a physisorption well depth which is much smaller than observed for bulk Pd(111) or an activation barrier to H$_2$ adsorption or both. The small sticking coefficient being due to a large change in the physisorption well depth seems unreasonable because of the small range of values predicted for the well depth for a large number of materials (0.8 - 3.6 kcal/mol) [1]. Conversely, TPD results show that the chemisorption state is destabilized on the $\theta_{\text{Pd}} = 1$ film since the desorption temperature is only 250 K on the $\theta_{\text{Pd}} = 1$ film but is 346 K on a thick ($\theta_{\text{Pd}} \approx 50$) Pd film. This destabilization of the chemisorption state could cause an activation barrier to appear as can be seen by simply raising the chemisorption potential. We therefore draw the intersection of the physisorption and chemisorption well above the zero of potential energy creating an activation barrier to adsorption. Desorption from the $\alpha$ state is unaffected by depositing Pd on Ta(110). This is surprising because Pd hydride formation should be sensitive to the bulk electronic structure since Rh and Ag do not have these states [1]. The well depth for this state is therefore the same as for bulk Pd(111). Since the bulk of the sample is now Ta the barrier to diffusion into the bulk will be smaller and the energy of solution will be larger relative to bulk Pd.

For Cu [20], Ag [10], and Au [21] it is known that H$_2$ chemisorption is an activated process. This is thought to be due to the lack of d holes for these metals which serve to reduce the Pauli repulsion through s-d transfer [22]. Because the d bands of Cu, Ag and Au are filled, s-d rehybridization can not occur which causes
the Pauli repulsion to be high creating an activation barrier for chemisorption. A similar situation could be occurring for the $\theta_{pd} = 1$ film. Photoemission studies of Pd monolayers on Ta(110) have shown that the electronic structure of the Pd overlayer resembles a Group IB metal (Cu, Ag, Au) in that the d-band is narrowed and shifted to higher binding energies and the DOS at the Fermi level is reduced [5,23-26]. Additionally, theoretical calculations by Kumar and Bennemann [27] predict that the Pd monolayer d states are more filled relative to Pd(111). Because of this we feel it is very likely that there is a barrier to dissociative chemisorption and this is responsible for the low value of $S_{ads}$ on the $\theta_{pd} = 1$ film.

For a Pd thickness of $\theta_{pd} = 0.7$ the sticking coefficient is slightly lower than Ta(110) and the $\theta_{pd} = 1$ films and no desorption is observed from the $\alpha$ state. This could be due to the larger Pd-Pd distance for the pseudomorphic Pd monolayer. As the Pd film thickness increases above $\theta_{pd} = 1$, S also increases. For H$_2$ exposures at 100 K the increase in S is gradual and nearly proportional to the Pd film thickness. S does not reach its maximum value even for $\theta_{pd} = 50$ for H$_2$ exposures at 100 K. The low uptake rate is again due to the diffusion barrier which must be overcome for penetration into the bulk. However, the increase in S as the film thickness increases beyond $\theta_{pd} = 5$ is difficult to understand since we expect bulk properties for $\theta_{pd} \geq 5$. An increased number of defect sites in the Pd film could be responsible for this.

At 500 K the rate of absorption is high and S is representative of $S_{ads}$. As $\theta_{pd}$ increases above $\theta_{pd} = 1$ the increase in $S_{ads}$ is rapid but reaches its maximum value at approximately $\theta_{pd} = 5$. This is in agreement with previous results of Strongin and coworkers [2-5] and the chemisorption results reported for other molecules on Pd films on Ta(110). In general bulk Pd properties are found for films with $\theta_{pd} \geq 5$ [14,28]. However, while the data reported here are in excellent
agreement with that of Strongin and coworkers [2-5] we feel that the increased uptake rate observed for the thicker Pd films ($\theta_{\text{Pd}} \geq 5$) is due simply to an increased sticking coefficient rather than a lowering of the intrinsic barrier to diffusion into the bulk. We also feel that $S$ will reach an upper limit of 0.5 because it will be limited by the value of $S_{\text{ads}}$. This rules out $S = 1$ as suggested in their previous paper [3].

The dependence of populating the $\alpha$ state on annealing temperature raises interesting issues about the Pd film morphology. To explain the effect of annealing temperature on the population of the $\alpha$ state and gain information about the Pd film morphology we consider a kinetic model recently proposed by Kay et al. [29]. Within the framework of this model H$_2$ molecules impinging on the surface can be trapped into a mobile precursor state. H$_2$ molecules in the mobile precursor state can then diffuse across the surface, encounter a defect site, and absorb. Alternatively, molecules in the precursor state can leave the surface by desorbing. In addition to these processes, molecules which directly impact with a defect site may absorb. For bulk Pd(111), absorption into the bulk occurs only after the chemisorption state ($\beta$ state) is saturated, and it has been shown that there is no exchange between hydrogen atoms adsorbed in the $\beta$ state and hydrogen atoms in the $\alpha$ state [30]. Because of this the chemisorption state can be ignored. Thus, there are two routes to absorption into the bulk, precursor mediated absorption and direct absorption. This model predicts that for surfaces with low defect densities the absorption coefficient will be low due to most H$_2$ molecules in the precursor state desorbing before they have time to diffuse to a defect site. Increasing the defect density decreases the amount of time required for an H$_2$ molecule to diffuse to a defect site and therefore increases the absorption probability.

Using this model we can gain information about the Pd film morphology by considering the amount of H$_2$ desorption from the $\alpha$ state. At 100 K a large amount
of $H_2$ is observed to desorb from the $\alpha$ state for the $\theta_{Pd} = 3$ films. This implies that the Pd film has a large number of defects. This is not surprising and is likely due to a lack of sufficient thermal energy for the Pd atoms to diffuse across the surface. As the Pd film is annealed the defect density decreases and the probability for population of the $\alpha$ state decreases. Between 400 and 600 K the defect density on the Pd films is low enough that the $H_2$ molecules in the precursor state no longer have a long enough lifetime to diffuse to a defect site and absorb into the $\alpha$ state. At an annealing temperature of 700 K, desorption from the $\alpha$ state is again observed. This is likely due to three dimensional clusters forming which are large enough to populate the $\alpha$ state. These clusters persist until 1000 K. However, by 900 K alloy formation begins to occur and this gradually reduces the size and number of clusters on the surface. This leads to the $\alpha$ state vanishing by 1100 K.

Previous AES measurements of a $\theta_{Pd} = 3$ film show that it is stable between 100 and 350 K and LEED observations show a sharpening of the beat pattern over this temperature range [14]. This implies that the long range order of the Pd film increases as it is annealed and in turn causes the decrease in the population of the $\alpha$ state. Between 350 and 800 K a gradual decrease in the Pd AES signal intensity is observed and has been attributed to formation of 3D crystallites on top of the first Pd monolayer. It may at first be somewhat surprising that we observe no desorption from the $\alpha$ state between 400 and 600 K when 3D crystallites are on the surface. However, Kay et al. [29] have pointed out that the surface density of defects responsible for absorption into the $\alpha$ state was only $5.39 \times 10^{10}$ defects/cm$^2$ on a Pd(111) single crystal. This is significantly smaller than the density of typical surface morphological imperfections such as steps or kinks, which implies that not every defect will be active for hydrogen absorption. We can then say that for Pd films, 3D crystallites can not be simply equated with active defects. Between 700
and 800 K desorption from the α state increases. This could be due to agglomeration of smaller crystallites into larger crystallites which creates active defect sites. At 850 to 1000 K a rapid drop in the Pd AES signal occurs which is likely due to alloy formation. This is where the second decrease in H₂ desorption from the α state is observed and we propose that the decrease is due to the formation of a Pd-Ta alloy which can no longer populate the α state.

Brief reports of H₂ TPD experiments from Pd films deposited on Mo(100), W(100), and W(110) have also been published. On Mo(100), hydrogen chemisorption clearly occurs on the Pd monolayer. Similar to the current work, a destabilization of the H-Pd chemisorption bond was observed for a Pd monolayer on Mo(100) relative to thick (≥ 20) Pd films. A decrease in the H₂ sticking coefficient was also observed for the Pd monolayer relative to thick Pd films. Thus, for Pd films on the Mo(100) surface it appears that H₂ chemisorption is similarly affected as in the current work but the extent of the effects is not as large. The α state was also observed for Pd/Mo(100) but only for θₚd ≥ 5. This could be due to the film preparation procedures which included an anneal to 450 K prior to exposure to H₂.

On a W(110) surface, H₂ TPD from a monolayer Pd film showed the presence of a chemisorbed hydrogen state, which desorbed at a higher temperature (400 K) than the chemisorbed state for H₂ adsorbed on Pd(111) [9], and a high temperature state (510 K) ascribed to interfacial hydrogen [31]. As the Pd film thickness was increased, the intensity of the chemisorbed H₂ state decreased and two new states were observed at 200 and 275 K. These were attributed to desorption of H₂ from a hydride phase and the surface of three dimensional clusters of Pd respectively. The desorption temperature of the interfacial hydrogen remained constant as the film thickness increased. For a Pd monolayer on W(100) an interfacial H₂ desorption state was observed at 525 K and a chemisorbed state was
seen at 350 K. As the Pd film thickness increased the chemisorption state shifted down in temperature to 300 K. No well-developed Pd-hydride state was observed but a small shoulder at 200 K was attributed to Pd-hydride formation for films thicker than one monolayer.

The differences in the $\alpha$ state for these surfaces compared to the present work are likely due to different Pd film preparation procedures and the fact that hydrogen will not penetrate into the bulk of Mo or W under the experimental conditions used. The destabilization of the H-Pd bond seen here on Ta(110) is also seen on Mo(100) although to a lesser extent. This is consistent with the results of CO chemisorption which also show a stronger effect for Pd films on Ta(110) [14] compared to Pd films on Mo(100) [32]. The result for $\text{H}_2$ adsorption on W(110) and W(100) are perplexing. For the Pd monolayer on these surfaces the H-Pd chemisorption bond strength seems to be increased relative to bulk Pd. However, the CO chemisorption properties of the Pd monolayer on W(100) [31] and W(110) [31,33] are very similar to the CO chemisorption properties of a Pd monolayer on Mo(100) and Ta(110). This suggests that a reinvestigation of the W surfaces using the same Pd film preparation procedures as used here may be in order.

8.5 Summary

Pd films deposited on Ta(110) show strongly modified adsorption and absorption properties for $\text{H}_2$ when compared to bulk Pd. The Pd monolayer shows the largest effects with a small sticking coefficient for $\text{H}_2$ of 0.04 and the absence of hydrogen chemisorbed on Pd. As the Pd film thickness increases bulk Pd properties are regained as evidenced by an increased sticking coefficient and desorption of $\text{H}_2$ from a Pd chemisorption state. The increased sticking coefficient increases the hydrogen uptake rate by more than a factor of 4 relative to clean Ta(110) for thick ($\theta_{\text{Pd}} \geq 5$) Pd films. We also observe population of the low temperature hydride
state, denoted as $\alpha$, even for the $\theta_{\text{Pd}} = 1$ film. The amount of H$_2$ desorption from this state increases with increasing Pd film thickness and occurs at the same temperature as observed for bulk Pd(111). Population of the $\alpha$ state was found to be strongly dependent on the Pd film preparation procedures suggesting that, similar to bulk Pd(111), defects are important in the absorption kinetics.
REFERENCES FOR CHAPTER VIII


CHAPTER IX

CYCLOTRIMERIZATION OF C₂H₂ AND CHEMISORPTION OF BENZENE ON ULTRATHIN Pd FILMS ON Ta(110)

9.1 Introduction

The cyclotrimerization of acetylene to benzene is an interesting chemical reaction which has been studied extensively on Pd surfaces. It has been shown to occur in UHV and at atmospheric pressures [1-5]. The reaction mechanism is thought to involve a sequential C₂ → C₄ → C₆ process which does not involve any C-C or C-H bond cleavage. There appears to be a threshold C₂H₂ coverage necessary for the reaction to occur and on the clean Pd(111) surface the maximum amount of acetylene to benzene conversion is no greater than 25%. The amount of conversion can be increased by the addition of coadsorbates [6,7]. Reactively-formed C₆H₆ desorbs from the Pd(111) surface from states at 250 and 500 K. These have been attributed to "tilted" benzene species and a flat-lying benzene species respectively [4].

This reaction has also been recently studied on Pd films on Au(111) and Pd-Au surface alloys [8]. While the Au(111) surface is inert towards acetylene cyclotrimerization the reaction is observed on the Pd films. The extent of the reaction was found to be dependent on the Pd film morphology with the reaction occurring to a larger extent on smooth films than on rough films.

In this chapter results are presented for C₂H₂ and C₆H₆ chemisorption on ultrathin Pd films deposited on Ta(110). We find that the cyclotrimerization of acetylene to benzene does occur on these films. Only a flat lying C₆H₆ species is
formed on the Pd monolayer while both flat and tilted species are seen for thicker Pd films. In addition, only half as much C$_6$H$_6$ is formed on the Pd monolayer relative to thick ($\theta_{Pd} = 5$) films. Benzene desorption following benzene exposure initially occurs at 400 K on the Pd monolayer while on thick ($\theta_{Pd} = 5$) Pd films benzene desorbs at 500 K. This establishes that benzene is more weakly bound on the $\theta_{Pd} = 1$ film.

9.2 Experimental Information

The apparatus used in these experiments is described in chapter II. The base pressure of the chamber was $1 \times 10^{-10}$ torr. All C$_2$H$_2$ and C$_6$H$_6$ adsorption experiments were performed on Pd films which had been annealed to 400 K in order to avoid (as much as possible) any changes in the Pd film structure during TPD experiments. The heating rate used during TPD experiments was 5 K/sec. Pd coverages were derived from AES and LEED observations, with $\theta_{Pd} = 1$ corresponding to a Pd coverage approximately equal to the Pd(111) surface atom density [9].

9.3 Results

9.3.1 C$_2$H$_2$ Chemisorption on a monolayer Pd film, $\theta_{Pd} = 1$

Figure 9.1 shows TPD spectra following C$_2$H$_2$ exposures on a $\theta_{Pd} = 1$ film at 91 K. The desorption products observed are C$_2$H$_2$, C$_6$H$_6$, C$_2$H$_4$, and H$_2$. C$_2$H$_2$ exposures of 0.005 L lead to a single desorption state of C$_2$H$_2$, labeled $\alpha_1$, at 265 K with a small shoulder on the low temperature side (fig. 9.1a). Upon increasing the exposure to 0.01 L the desorption state at 265 K increases in size and a second desorption state, labeled $\alpha_2$, is observed at 180 K. Increasing C$_2$H$_2$ exposure causes the $\alpha_2$ desorption state to increase in size and broaden towards lower temperature.
Figure 9.1a-b TPD spectra from a $\theta_{pd} = 1$ film as a function of C$_2$H$_2$ exposure at 91 K. (a) C$_2$H$_2$ TPD spectra, (b) C$_6$H$_6$ TPD spectra.
Figure 9.1c-d TPD spectra from a $\theta_{pd} = 1$ film as a function of $C_2H_2$ exposure at 91 K. (c) $C_2H_4$ TPD spectra, (d) $H_2$ TPD spectra.
Figure 9.1b shows TPD spectra for reactively-formed C\textsubscript{6}H\textsubscript{6} following C\textsubscript{2}H\textsubscript{2} exposure. No benzene production is observed for a 0.005 L C\textsubscript{2}H\textsubscript{2} exposure. Upon increasing the C\textsubscript{2}H\textsubscript{2} exposure to 0.01 L a small C\textsubscript{6}H\textsubscript{6} desorption state is observed at 400 K. Increases in the C\textsubscript{2}H\textsubscript{2} exposure up to 1 L increase the amount of C\textsubscript{6}H\textsubscript{6} desorption. Above this exposure no significant change in the amount of C\textsubscript{6}H\textsubscript{6} desorption is observed. C\textsubscript{2}H\textsubscript{4} desorption is also observed following C\textsubscript{2}H\textsubscript{2} exposures. This is shown in fig. 9.1c. Following a C\textsubscript{2}H\textsubscript{2} exposure of 0.005 L there are C\textsubscript{2}H\textsubscript{4} desorption states observed at 200, 300, and 430 K. Increasing C\textsubscript{2}H\textsubscript{2} exposure causes the desorption state at 200 K to grow in size and broaden towards lower temperature. The desorption state at 300 K becomes a broad plateau as the C\textsubscript{2}H\textsubscript{2} exposure increases obscuring the peak at 430 K.

We have also monitored the desorption of H\textsubscript{2} following C\textsubscript{2}H\textsubscript{2} exposures. Unfortunately, H\textsubscript{2} adsorption on Pd films deposited on Ta(110) is complicated by penetration of hydrogen into the bulk as discussed in chapter VIII. This complicates the analysis since we are unable to use the H\textsubscript{2} desorption signal to help quantify the desorption yields of the various products. However, fig. 9.1d shows that there is no desorption of H\textsubscript{2} from the Pd film attributable to chemisorbed hydrogen or the decomposition of reaction intermediates. There is however a substantial amount of H\textsubscript{2} desorption from the bulk of the crystal. This is likely due to decomposition of C\textsubscript{2}H\textsubscript{2} on the clean edges and crystal back followed by penetration of hydrogen into the bulk.

Figures 9.2a-d show similar TPD spectra for C\textsubscript{2}H\textsubscript{2} exposures on a $\theta\textsubscript{Pd} = 1$ film at 175 K. C\textsubscript{2}H\textsubscript{2} exposures were performed at this temperature to allow a more direct comparison to previous work on Pd(111) single crystals [1-4]. Initially the $\alpha_1$ desorption state is populated similarly to C\textsubscript{2}H\textsubscript{2} exposures at 91 K. As the C\textsubscript{2}H\textsubscript{2} exposure is increased the $\alpha_2$ state begins to be populated. The $\alpha_1$ and $\alpha_2$ states both
Figure 9.2a-b TPD spectra from a $\theta_{pd} = 1$ film as a function of $C_2H_2$ exposure at 175 K. (a) $C_2H_2$ TPD spectra, (b) $C_6H_6$ TPD spectra.
Figure 9.2c-d TPD spectra from a $\theta_{\text{Pd}} = 1$ film as a function of C$_2$H$_2$ exposure at 175 K. (c) C$_2$H$_4$ TPD spectra, (b) H$_2$ TPD spectra.
grow in size as the C$_2$H$_2$ exposure is increased reaching maximum size at an C$_2$H$_2$ exposure of 1 L. Increasing the C$_2$H$_2$ exposure further causes no increase in the amount of C$_2$H$_2$ desorbing. A single C$_6$H$_6$ desorption state is observed at 400 K following C$_2$H$_2$ exposures at 175 K (fig. 9.2b), which is similar to the C$_2$H$_2$ exposures at 91 K. However, a 0.1 L C$_2$H$_2$ exposure is required before C$_6$H$_6$ desorption is observed, a ten-fold increase relative to C$_2$H$_2$ exposures at 91 K. The amount of C$_6$H$_6$ desorbing saturates after a 1 L C$_2$H$_2$ exposure. C$_2$H$_4$ desorption following C$_2$H$_2$ exposure at 175 K is initially characterized by a small desorption state centered around 300 K (fig. 9.2c). At a C$_2$H$_2$ exposure of 1 L a second C$_2$H$_4$ desorption state is populated at 230 K. No H$_2$ desorption is detected other than that desorbing from the bulk of the sample which is similar to C$_2$H$_2$ exposures at 91 K.

Figure 9.3 shows a comparison of the TPD areas of the products. The amount of C$_2$H$_2$ reversibly adsorbed at 91 K is much larger than that observed at 175 K. The amount of C$_2$H$_4$ desorbing following C$_2$H$_2$ exposures at 91 K is also much larger than seen for C$_2$H$_2$ exposures at 175 K. Conversely, the amount of C$_6$H$_6$ desorption is insensitive to the C$_2$H$_2$ exposure temperature on the \( \theta_{Pd} = 1 \) film. Thus, it appears that the additional C$_2$H$_2$ which is adsorbed at 91 K does not play an important role in the production of C$_6$H$_6$. The total amount of C$_6$H$_6$ formed is quite low. Based on experiments to be presented below, the amount desorbed is only 1% of the total amount of benzene desorbing following benzene exposure on a \( \theta_{Pd} = 1 \) film.

9.3.2 C$_2$H$_2$ Chemisorption on Pd Films of Increasing Thickness

Figure 9.4 shows TPD spectra following 1 L C$_2$H$_2$ exposures at 175 K as a function of Pd film thickness. As described above, the \( \theta_{Pd} = 1 \) film shows C$_2$H$_2$ desorption from the \( \alpha_1 \) and \( \alpha_2 \) desorption states at 280 and 210 K respectively.
Comparison of TPD Areas for C$_2$H$_2$ exposures at 91 and 175 K on $\theta_{Pd} = 1$ films

Figure 9.3 Comparison of TPD areas for desorption products following C$_2$H$_2$ exposures on a $\theta_{Pd} = 1$ film at 91 and 175 K. Note that the C$_2$H$_2$ TPD area for exposures at 91 K has been divided by 10 while the benzene TPD area for both exposure temperatures has been multiplied by 10.
Figure 9.4 a-b TPD spectra following 1 L C$_2$H$_2$ exposures at 175 K on several Pd films. (a) C$_2$H$_2$ TPD spectra, (b) C$_6$H$_6$ TPD spectra.
Figure 9.4 c-d  TPD spectra following 1 L C$_2$H$_2$ exposures at 175 K on several Pd films. (a) C$_2$H$_2$ TPD spectra, (b) C$_6$H$_6$ TPD spectra.
A drastic reduction in the amount of C$_2$H$_2$ desorbing from these states is observed on the $\theta_{pd} = 2$ film and a new, broad C$_2$H$_2$ desorption state centered around 370 K appears. Increasing the film thickness to $\theta_{pd} = 3$ causes the $\alpha_1$ and $\alpha_2$ C$_2$H$_2$ desorption states to completely disappear while the broad desorption state at 370 K is slightly enhanced. The overall shape of the C$_2$H$_2$ desorption peak for the $\theta_{pd} = 5$ film is similar to that observed for the $\theta_{pd} = 3$ film but a slight increase in the amount of C$_2$H$_2$ desorbing is observed.

Figure 9.4b shows benzene TPD spectra following 1 L C$_2$H$_2$ exposures at 175 K as a function of Pd film thickness. Dramatic changes are observed for the desorption of C$_6$H$_6$ as the Pd film thickness is increased. On the $\theta_{pd} = 1$ film a single C$_6$H$_6$ desorption state is observed at 400 K. C$_6$H$_6$ desorption states are seen at 300 and 480 K on the $\theta_{pd} = 2$ film. There is also a shoulder on the low temperature side of the 480 K peak at 430 K. These C$_6$H$_6$ desorption peaks have shifted to 250 and 500 K at a Pd film thickness of $\theta_{pd} = 3$. The peak at 250 K grows in size for a Pd film thickness of $\theta_{pd} = 5$, but the peak at 500 K decreases in size.

Significant changes are also observed for C$_2$I$_4$ desorption as the Pd film thickness is increased (fig. 9.4c). On the $\theta_{pd} = 1$ film C$_2$I$_4$ desorption peaks are observed at 230 and 300 K. Increasing the Pd film thickness to $\theta_{pd} = 2$ causes a large decrease in the amount of C$_2$I$_4$ desorbing from these states and the appearance of a new C$_2$I$_4$ desorption state at 445 K. Increasing the Pd film thickness further causes the two low temperature C$_2$I$_4$ desorption states to disappear and the desorption peak at 445 K shifts up in temperature to 470 K.

No desorption of H$_2$ from the Pd film attributable to chemisorbed hydrogen or the decomposition of reaction intermediates is observed until a Pd thickness of $\theta_{pd} = 5$ is reached (fig. 9.4d). At this thickness a new H$_2$ desorption peak is
observed at 430 K. This peak is due to the decomposition of a hydrocarbon fragment which in turn causes H₂ desorption to occur.

The TPD areas of the desorption products are shown in fig. 9.5 as a function of the Pd film thickness. This shows that approximately twice as much C₂H₂ is reversibly adsorbed on the θ_pd = 1 film than on the θ_pd = 5 film at 175 K. In contrast, approximately half as much benzene desorbs from the θ_pd = 1 film when compared to the θ_pd = 5 film. The amount of C₂H₄ desorption decreases by about one third as the film thickness increases from θ_pd = 1 to θ_pd = 5 while an abrupt increase in the H₂ desorption is seen on the θ_pd = 5 film.

9.3.3 C₂H₂ Chemisorption on a 5 Layer Thick Film, θ_pd = 5

The TPD spectra following C₂H₂ exposures at 91 K on a θ_pd = 5 film are shown in fig. 9.6 a-d. Following a 0.01 L C₂H₂ exposure only a small spike due to desorption of C₂H₂ from the heating wires is observed. With increasing C₂H₂ exposure a C₂H₂ desorption peak grows in at 140 K. This peak broadens towards higher temperature as the C₂H₂ exposure is increased and a long desorption tail is observed for a C₂H₂ exposure greater than 1 L. The state at 140 K does not appear to saturate even for 4 L exposures indicating multilayer formation. Figure 9.6b shows C₆H₆ TPD spectra monitored concurrently with the C₂H₂ TPD spectra. In contrast to the θ_pd = 1 film, no benzene desorption is observed following C₂H₂ exposures at 91 K on the θ_pd = 5 film. Desorption of C₂H₄ is shown in fig. 9.6c. A small C₂H₄ desorption peak is observed at 250 K with a second, larger peak at 465 K for the 0.01 L C₂H₂ exposure. After a C₂H₂ exposure of 0.1 L both of these states have grown in size. A new desorption peak is observed at 150 K for a C₂H₂ exposure of 1 L. Increasing the C₂H₂ exposure further causes no changes in the C₂H₄ TPD spectrum. H₂ TPD spectra following C₂H₂ exposures at 91 K on a θ_pd = 5 film are shown in fig. 9.6d. A slight increase in the amount of H₂ desorbing
Figure 9.5 Comparison of TPD areas of the desorption products as a function of Pd film thickness following a 1 L C$_2$H$_2$ exposure at 175 K. Note that the benzene TPD areas are multiplied by 10.
Figure 9.6a-b TPD spectra from a $\theta_{pd} = 5$ film as a function of C$_2$H$_2$ exposure at 91 K. (a) C$_2$H$_2$ TPD spectra, (b) C$_6$H$_6$ TPD spectra
Figure 9.6c-d TPD spectra from a $\theta_{\text{Pd}} = 5$ film as a function of $\text{C}_2\text{H}_2$ exposure at 91 K. (a) $\text{C}_2\text{H}_4$ TPD spectra, (b) $\text{H}_2$ TPD spectra.
is observed at 350 K for a 0.01 L C2H2 exposure. Increasing the C2H2 exposure to 0.1 L causes the appearance of a distinct peak at 420 K. A slight shift to 450 K is observed for this peak for a 1 L C2H2 exposure. Increasing the C2H2 exposure further causes no changes in the H2 TPD spectrum.

TPD spectra following C2H2 exposures on a θpd = 5 film at 175 K are shown in fig. 9.7. No desorption of C2H2 is observed (fig. 9.7a) for 0.05 L C2H2 exposures. Increasing the exposure to 0.1 L causes a small C2H2 desorption peak to become visible at 400 K. This peak increases in size and broadens as the C2H2 exposure is increased, and appears to saturate after a 1 L C2H2 exposure. Benzene desorption following C2H2 exposure on a θpd = 5 film at 175 K is shown in fig. 9.7b. No benzene is observed to desorb for 0.05 L C2H2 exposures. Increasing the C2H2 exposure to 0.1 L causes the appearance of a benzene desorption peak at 250 K. The benzene desorption state at 250 K has doubled in size and a new desorption state is seen at 500 K for a C2H2 exposure of 1 L. Further increases in the C2H2 exposure cause no changes in the benzene desorption features. The C2H4 TPD spectra following C2H2 exposures on a θpd = 5 film at 175 K are shown in fig. 9.7c. A single desorption peak at 465 K is observed for a 0.05 L C2H2 exposure. Increasing the C2H2 exposure to 0.1 L increases the size of this peak but the temperature remains constant. Further increases in the C2H2 exposure cause no changes in the C2H4 TPD spectrum. Figure 9.7d shows the H2 TPD spectra following C2H2 exposures. A small H2 desorption state is observed at 420 K for a 0.05 L C2H2 exposure. Increasing the C2H2 exposure to 0.1 L increases the size of this peak and causes a slight shift of the peak maximum to higher temperatures. A further increase in the size of the desorption peak is observed for a 1 L C2H2 exposure and the peak maximum has shifted to 450 K.
Figure 9.7a-b TPD spectra from a \( \theta_{pd} = 5 \) film as a function of \( \mathrm{C}_2\mathrm{H}_2 \) exposure at 175 K. (a) \( \mathrm{C}_2\mathrm{H}_2 \) TPD spectra, (b) \( \mathrm{C}_6\mathrm{H}_6 \) TPD spectra.
Figure 9.7c-d TPD spectra from a $\theta_{pd} = 5$ film as a function of C$_2$H$_2$ exposure at 175 K. (c) C$_2$H$_4$ TPD spectra, (d) H$_2$ TPD spectra.
Comparison of TPD areas for desorption products following C\textsubscript{2}H\textsubscript{2} exposures on a θ\textsubscript{pd} = 5 film at 91 and 175 K. Note that the C\textsubscript{2}H\textsubscript{2} TPD area for exposures at 91 K and the H\textsubscript{2} TPD area for both exposure temperatures has been divided by 10 while the benzene TPD area for both exposure temperatures has been multiplied by 10.
Further increases in the C$_2$H$_2$ exposure causes no changes in the H$_2$ TPD spectrum.

Figure 9.8 compares the TPD areas of the desorption products from the $\theta_{\text{Pd}} = 5$ film following C$_2$H$_2$ exposures at 91 and 175 K. The amount of C$_2$H$_2$ reversibly adsorbed at 91 K is much larger than that observed at 175 K which is similar to the $\theta_{\text{Pd}} = 1$ film. Conversely, no C$_6$H$_6$ desorption is observed following C$_2$H$_2$ exposure at 91 K while a substantial amount desorbs following C$_2$H$_2$ exposure at 175 K. On Pd(111), C$_2$H$_2$ in a $\sqrt{3} \times \sqrt{3}$ R30$^\circ$ structure has been shown to be responsible for the formation of benzene [4]. The lack of benzene formation at 91 K could possibly be due to the additional adsorbed C$_2$H$_2$ interfering with the reaction through steric interactions or the lack of an ordered C$_2$H$_2$ layer at 91 K. Unfortunately, no studies on Pd(111) single crystals have been performed below 130 K so we are unable to determine if this is unique to the Pd film. The amount of C$_2$H$_4$ desorbing following C$_2$H$_2$ exposures at 91 K is slightly larger than seen for C$_2$H$_2$ exposures at 175 K.

We can also compare the relative product yields from the $\theta_{\text{Pd}} = 1$ and $\theta_{\text{Pd}} = 5$ films following exposures at 91 and 175 K. Figure 9.9 compares the TPD areas of the desorption products from the $\theta_{\text{Pd}} = 1$ and $\theta_{\text{Pd}} = 5$ films following exposures at 91 K. Initially, the amount of C$_2$H$_2$ reversibly adsorbed on the $\theta_{\text{Pd}} = 1$ film is more than ten times as large as the amount of C$_2$H$_2$ reversibly adsorbed on the $\theta_{\text{Pd}} = 5$ film. With increasing C$_2$H$_2$ exposure the difference in the amount of C$_2$H$_2$ reversibly adsorbed on the two films decreases, possibly due to contribution to the signal from background gas, and by an exposure of 4 L the amount of C$_2$H$_2$ reversibly adsorbed is nearly equal. As discussed above, no benzene formation is observed on the $\theta_{\text{Pd}} = 5$ film for C$_2$H$_2$ exposures at 91 K. In contrast, there is as much benzene formation for C$_2$H$_2$ exposures at 91 K as for C$_2$H$_2$ exposures at 175 K on the $\theta_{\text{Pd}} = 1$ film. This seems to rule out the lack of benzene
Figure 9.9  Comparison of TPD areas for desorption products following C\textsubscript{2}H\textsubscript{2} exposures on a \( \theta_{\text{pd}} = 1 \) and \( \theta_{\text{pd}} = 5 \) film at 91 K. Note that the C\textsubscript{2}H\textsubscript{2} TPD area and the H\textsubscript{2} TPD area for both film thicknesses has been divided by 10 while the benzene TPD area for both film thicknesses has been multiplied by 10.
formation on the $\theta_{\text{pd}} = 5$ film as being due to the additional benzene adsorbed at 91 K since we would then expect the same result on the $\theta_{\text{pd}} = 1$ film.

The amount of C$_2$H$_4$ desorbing from the $\theta_{\text{pd}} = 1$ film is much larger than observed for the $\theta_{\text{pd}} = 5$ film. It appears that when more C$_2$H$_2$ is reversibly adsorbed more C$_2$H$_4$ production occurs. On the $\theta_{\text{pd}} = 5$ film a distinct H$_2$ desorption peak is observed above the H$_2$ desorbing from the bulk. This is likely due to the decomposition of a hydrocarbon fragment to produce atomic hydrogen which then combines and desorbs as H$_2$. No such state is observed on the $\theta_{\text{pd}} = 1$ film. There are two possible reasons for this. First, it is possible that only a small amount of C$_2$H$_2$ decomposition occurs on the $\theta_{\text{pd}} = 1$ film. This is consistent with the increased propensity for reversible adsorption of C$_2$H$_2$ on the $\theta_{\text{pd}} = 1$ film relative to the $\theta_{\text{pd}} = 5$ film and with data presented in the next section involving consecutive TPD experiments. Alternatively, C-H bond cleavage could occur followed by hydrogen penetration into the bulk of the crystal. This is consistent with the fact that no chemisorbed hydrogen was observed following H$_2$ exposures on the $\theta_{\text{pd}} = 1$ film and that the heat of solution of hydrogen in Ta is larger than the heat of adsorption on Pd. Of course, both the smaller amount of C$_2$H$_2$ decomposition and the inability to populate a hydrogen chemisorbed state could play a role in the lack of an H$_2$ desorption state on the $\theta_{\text{pd}} = 1$ film.

Figure 9.10 compares the TPD areas of the desorption products from the $\theta_{\text{pd}} = 1$ and $\theta_{\text{pd}} = 5$ films following C$_2$H$_2$ exposures at 175 K. Initially, C$_2$H$_2$ exposures at 175 K result in much more C$_2$H$_2$ being reversibly adsorbed on the $\theta_{\text{pd}} = 1$ film when compared to the $\theta_{\text{pd}} = 5$ film. The amount of C$_2$H$_2$ desorbing from the $\theta_{\text{pd}} = 1$ film has nearly reached its maximum by a C$_2$H$_2$ exposure of 0.1 L and increased C$_2$H$_2$ exposure causes only a slight increase in the amount of C$_2$H$_2$.
Figure 9.10  Comparison of TPD areas for desorption products following $\text{C}_2\text{H}_2$ exposures on a $\theta_{\text{Pd}} = 1$ and $\theta_{\text{Pd}} = 5$ film at 175 K. Note that the $\text{H}_2$ TPD area for the $\theta_{\text{Pd}} = 5$ film has been divided by 10 while the benzene TPD area for both film thicknesses has been multiplied by 10.
desorbing. In contrast, the amount of $C_2H_2$ desorption from the $\theta_{pd} = 5$ film continues to increase for $C_2H_2$ exposures up to 2 L. Figure 9.10 also shows that approximately twice as much benzene desorbs from the $\theta_{pd} = 5$ film as the $\theta_{pd} = 1$ film for $C_2H_2$ exposures at 175 K. In contrast, the amount of $C_2H_4$ desorption from the $\theta_{pd} = 1$ film is about twice that from the $\theta_{pd} = 5$ film.

9.3.3 Consecutive TPD Experiments on a $\theta_{pd} = 1$ and $\theta_{pd} = 5$ Film

From the preceding discussion it appears that very little $C_2H_2$ decomposition occurs on the $\theta_{pd} = 1$ film while a substantial amount of decomposition occurs on the $\theta_{pd} = 5$ film. To further test this hypothesis we conducted consecutive TPD experiments on $\theta_{pd} = 1$ and $\theta_{pd} = 5$ films following 1 L $C_2H_2$ exposures at 175 K. The results for the $\theta_{pd} = 1$ film are shown in fig. 9.11a-d. Initially, the $\alpha_1$ and $\alpha_2$ $C_2H_2$ desorption states are observed clearly on the $\theta_{pd} = 1$ film (fig. 9.11a). The second $C_2H_2$ TPD spectrum from the $\theta_{pd} = 1$ film shows a slight broadening of $\alpha_2$ desorption state. This trend continues for the third and fourth TPD experiment. No other changes are evident and the $C_2H_2$ TPD area remains constant. The corresponding $C_6H_6$ TPD spectra are shown in fig. 9.11b. The first $C_6H_6$ TPD spectrum shows a single peak at 400 K. Only a slight decrease in the desorption temperature and size of the $C_6H_6$ TPD peak is observed for subsequent TPD experiments. The $C_2H_4$ TPD spectra from the $\theta_{pd} = 1$ film are shown in fig. 9.11c. The first TPD spectrum shows a peak at 230 K and a broad desorption state centered at 300 K. Performing consecutive TPD experiments serves to broaden the peak at 230 K and decrease the total amount of $C_2H_4$ desorbing. No changes are observed for the $H_2$ desorption signal for the consecutive TPD experiments.

The TPD spectra from a $\theta_{pd} = 5$ film following 1 L $C_2H_2$ exposures at 175 K are shown in fig. 9.12a-d. For the first TPD, $C_2H_2$ desorption occurs from a broad peak centered at 400 K. No substantial change in the $C_2H_2$ desorption spectra
Figure 9.11a-b Consecutive TPD spectra from a $\theta_{\text{Pd}} = 1$ film following 1 L $\text{C}_2\text{H}_2$ exposures at 175 K. (a) $\text{C}_2\text{H}_2$ TPD spectra, (b) $\text{C}_6\text{H}_6$ TPD spectra.
Figure 9.11c-d Consecutive TPD spectra from a $\theta_{Pd} = 1$ film following 1 L $C_2H_2$ exposures at 175 K. (c) $C_2H_4$ TPD spectra, (d) $H_2$ TPD spectra.
Figure 9.12a-b Consecutive TPD spectra from a $\theta_{Pd} = 5$ film following 1 L $C_2H_2$ exposures at 175 K. (a) $C_2H_2$ TPD spectra, (b) $C_6H_6$ TPD spectra.
Figure 9.12c-d  Consecutive TPD spectra from a $\theta_{\text{Pd}} = 5$ film following 1 L C$_2$H$_2$ exposures at 175 K. (c) C$_2$H$_4$ TPD spectra, (d) H$_2$ TPD spectra.
are observed as the TPD experiment is repeated. Benzene desorption occurs from peaks at 250 and 500 K for the first TPD. Repeating the TPD experiment causes the desorption peak at 250 K to broaden toward higher temperatures and the peak initially at 500 K to shift down to 450 K and increase in size. Repeating the TPD for a third time results in no C₆H₆ desorption from the high temperature state and a large decrease in the size of the 250 K peak. A further decrease in the amount of C₆H₆ desorbing from the low temperature peak is observed for the fourth TPD. C₂H₄ desorption is observed from a peak at 460 K initially. This peak decreases in size for the second TPD and disappears following the third TPD. An H₂ desorption peak is observed at 420 K for the first TPD while subsequent TPD experiments show only H₂ desorption from the bulk of the crystal.

Figure 9.13 shows a comparison of the TPD areas of the products for each of the four TPD experiments on the θ₋₁ = 1 and θ₋₁ = 5 films. For both the θ₋₁ = 1 and θ₋₁ = 5 films the amount of C₂H₂ desorption remains approximately constant as the TPD experiment is repeated with twice as much C₂H₂ desorbing from the θ₋₁ = 1 film as the θ₋₁ = 5 film. For the θ₋₁ = 1 film the amount of benzene desorption gradually decreases as the TPD experiment is repeated and by the fourth TPD there is about 10% less C₆H₆ desorption. In contrast, on the θ₋₁ = 5 film the amount of benzene desorbing during the second TPD experiment is more than twice the amount desorbing during the first TPD experiment. The amount of benzene desorption decreases for the third TPD experiment and almost no benzene desorption is seen during the fourth TPD experiment. The observed trend on the θ₋₁ = 5 film is likely due to the small amount of residual carbon adsorbed on the surface following the first TPD acting in a similar fashion as other additives [6,7] and promoting the cyclotrimerization reaction. As the coverage of adsorbed carbon is increased the amount of benzene formation is reduced due to site blocking.
Figure 9.13 TPD areas of desorption products for consecutive TPD experiments on $\theta_{\text{PD}} = \theta_{\text{PD}} = 5$ film. Note that the C$_6$H$_6$ TPD areas have been multiplied by 10 and the H$_2$ TPD areas on the $\theta_{\text{PD}} = 5$ film have been divided by 10.
A decrease in the amount of C$_2$H$_4$ desorbing is observed after the first TPD for the $\theta_{pd} = 1$ film but the amount of C$_2$H$_4$ desorbing from the $\theta_{pd} = 1$ film remains constant after that. Concurrent with the large increase in benzene desorption seen on the $\theta_{pd} = 5$ film for the second TPD we see a large decrease in the amount of C$_2$H$_4$ desorption during the second TPD on the $\theta_{pd} = 5$ film.

### 9.3.4 C$_6$H$_6$ Chemisorption on $\theta_{pd} = 1$ and $\theta_{pd} = 5$ Films

Figure 9.14 shows benzene TPD spectra following benzene exposures on a $\theta_{pd} = 1$ film at 91 K. A 0.01 L C$_6$H$_6$ exposure leads to a single C$_6$H$_6$ desorption peak at 400 K. This peak is attributed to desorption of chemisorbed benzene. No C$_2$H$_2$ desorption was observed. Using Redhead analysis [10] and assuming a desorption order of 1 and a value for the preexponential factor of $10^{13}$ s$^{-1}$, an activation energy of desorption, $E_a$, of 24 kcal/mol is determined. As the C$_6$H$_6$ exposure is increased the C$_6$H$_6$ desorption peak increases in size, shifts towards lower temperature, and becomes very broad. The width of this peak indicates that more weakly bound benzene is adsorbed at the higher exposures, possibly a "tilted" benzene species. For an exposure of 0.12 L a new peak begins to emerge at 180 K. With increasing exposure this peak increases in size, does not saturate, and is attributed to multilayer formation.

Figure 9.15 shows benzene desorption following benzene exposures on a $\theta_{pd} = 5$ film at 91 K. No C$_6$H$_6$ desorption is observed until a benzene exposure of 0.025 L. This results in a small C$_6$H$_6$ desorption peak at 495 K in good agreement with results for desorption of chemisorbed benzene from bulk Pd(111) surfaces [12]. Using Redhead analysis [10] under the same assumptions mentioned above yields an $E_a$ of 30 kcal/mol. This peak increases in size as the C$_6$H$_6$ exposure is increased, broadening towards lower temperature, but retaining a nearly constant
Figure 9.14  \( \text{C}_6\text{H}_6 \) TPD Spectra following \( \text{C}_6\text{H}_6 \) exposures on a \( \theta_{\text{Pd}} = 1 \) film at 91 K.
Figure 9.15 \( \text{C}_6\text{H}_6 \) TPD Spectra following \( \text{C}_6\text{H}_6 \) exposures on a \( \theta_{\text{Pd}} = 5 \) film at 91 K.
desorption temperature. At a C₆H₆ exposure of 0.04 L desorption from the multilayer is observed at 180 K.

Figure 9.16 shows a direct comparison of the TPD spectra from a θₚd = 1 film and θₚd = 5 film. These particular spectra were chosen to illustrate the dramatic difference in the amount of reversibly adsorbed benzene for the two film thicknesses. The spectrum shown by the dashed curve represents benzene desorbed from a θₚd = 1 film for an exposure just below that needed to produce the multilayer desorption state on this surface, i.e., the maximum amount of chemisorbed benzene. The spectrum shown by the solid line represents benzene desorption from a θₚd = 5 film which already shows the multilayer state. It is easily seen that the amount of reversibly adsorbed benzene on the θₚd = 1 film is more than 10 times the amount of reversibly adsorbed benzene on the θₚd = 5 film.

A comparison of the benzene TPD areas as a function of benzene exposure is shown in figure 9.17. This shows the large difference in the benzene exposure required to populate the multilayer state for the θₚd = 1 and θₚd = 5 films. For the θₚd = 5 film a 0.04 L benzene exposure is required while for the θₚd = 1 film a 0.14 L benzene exposure is required. Taken together with the large amount of reversibly chemisorbed benzene on the θₚd = 1 film this indicates that much more benzene can be packed on the surface of the θₚd = 1 film when compared to the θₚd = 5 film. A possible explanation for this is that the less strongly bound benzene on the θₚd = 1 film is a tilted species. This is supported by the low desorption temperature (200 K for the leading edge of the peak) which agrees with the low temperature desorption of reactively-formed benzene which has been attributed to a tilted species [4]. This adsorption path is not available to benzene molecules on the θₚd = 5 film due to the stronger Pd-benzene bond in this case.
Comparison of \( \text{C}_6\text{H}_6 \) TPD Spectra From a \( \theta_{\text{Pd}} = 1 \) and \( \theta_{\text{Pd}} = 5 \) Film

Figure 9.16 Comparison of the \( \text{C}_6\text{H}_6 \) TPD spectra from a \( \theta_{\text{Pd}} = 1 \) and a \( \theta_{\text{Pd}} = 5 \) film showing the large difference in the population of the chemisorption state.
Figure 9.17  Comparison of the $\text{C}_6\text{H}_6$ TPD area as a function of $\text{C}_6\text{H}_6$ exposure on a $\theta_{\text{Pd}} =$ 1 and $\theta_{\text{Pd}} =$ 5 film. The exposure temperature was 91 K.
9.4 Discussion

The results presented in this chapter clearly show that Pd films deposited on Ta(110) have altered chemisorption properties for C₂H₂ and C₆H₆ when compared to bulk Pd(111). As with the other molecules studied, the largest effects are observed on the θ_Pd = 1 film. For C₂H₂ the propensity for reversible adsorption is greatly increased on the θ_Pd = 1 film relative to bulk Pd(111). Based on consecutive TPD experiments almost 100% of the C₂H₂ is removed (including reaction to form other desorption products) from the surface by 500 K. In contrast, XPS measurements for C₂H₂ adsorbed on Pd(111) at 300 K indicate that only 20% of the carbon on the surface is removed by 650 K [2]. However, it does not appear that the strength of the C₂H₂-Pd bond is weakened substantially on the Pd monolayer relative to bulk Pd(111). We observe C₂H₂ desorption states at 180 and 265 K while Gentle and Muetterties [3] report C₂H₂ desorption peaks at 188 and 300 K.

In addition to desorption of C₂H₂, C₂H₄ and C₆H₆ are reactively-formed and cause the removal of C₂H₂ from the surface. The cyclotrimerization of C₂H₂ to form benzene appears to be a relatively minor reaction path on the θ_Pd = 1 film. When referenced to the TPD area of C₆H₆ from C₆H₆ exposures the amount of reactively-formed C₆H₆ which desorbs is only 1% of a monolayer. The desorption of reactively-formed benzene does not appear to be reaction rate limited since it desorbs at the same temperature as C₆H₆ from C₆H₆ exposures. This has also been suggested for bulk Pd(111) [2].

C₂H₂ desorption from thick (θ_Pd = 5) Pd films does not appear to resemble C₂H₂ desorption from bulk Pd(111). On the θ_Pd = 5 film C₂H₂ desorption following C₂H₂ exposures at 175 K occurs from a very broad peak centered at 400 K. For C₂H₂ exposures on bulk Pd(111) at 175 K Gentle and Muetterties observe C₂H₂ desorption peaks at 188 and 300 K [3]. The broad desorption state we observe may indicate acetylene-induced morphology changes occurring as the surface
is heated during a TPD experiment. Desorption of reactively-formed benzene from the $\theta_{\text{Pd}} = 5$ films is very similar to that observed on bulk Pd(111). In both cases desorption peaks are observed at 250 and 500 K. The main difference seen for the Pd films is that most of the benzene formed desorbs from the peak at 250 K whereas on bulk Pd(111) nearly equal amounts were desorbed from both peaks [1-4]. This difference is likely due to structural features of the thin film either preventing the formation of a flat lying benzene or preventing its desorption from the surface.

Films of intermediate thickness ($\theta_{\text{Pd}} = 2$ and $\theta_{\text{Pd}} = 3$) appear to have some characteristics of both the $\theta_{\text{Pd}} = 1$ film and $\theta_{\text{Pd}} = 5$ film. C$_2$H$_2$ desorption from a $\theta_{\text{Pd}} = 2$ film shows both the low temperature $\alpha_1$ and $\alpha_2$ states as well as desorption from the broad peak at 400 K. C$_2$H$_4$ desorption from $\theta_{\text{Pd}} = 2$ and $\theta_{\text{Pd}} = 3$ films also shows characteristics of both the $\theta_{\text{d}} = 1$ and $\theta_{\text{Pd}} = 5$ film. Benzene desorption from $\theta_{\text{Pd}} = 2$ and $\theta_{\text{Pd}} = 3$ films mostly resembles desorption from the $\theta_{\text{Pd}} = 5$ film whereas H$_2$ desorption is more like a $\theta_{\text{Pd}} = 1$ film. Thus, it appears that there is some tuning of the chemisorption properties as the film thickness is increased but this may be due to a range of thicknesses being available due to surface roughness.

Chemisorption studies of C$_2$H$_2$ have also been carried out on Pd films on Mo(100) and are presented in chapter VI. Similar to the results presented in this chapter for Pd/Ta(110), we do not find a large change in the C$_2$H$_2$-Pd bond strength for C$_2$H$_2$ adsorbed on the Pd monolayer film on Mo(100). Another similarity is that C$_2$H$_2$ desorption from thick Pd films on Mo(100) also does not resemble desorption from the respective bulk Pd surface. However, unlike Pd/Ta(110) no C$_6$H$_6$ or C$_2$H$_4$ desorption was observed following C$_2$H$_2$ exposures on Pd/Mo(100). The lack of C$_6$H$_6$ formation is not surprising. The C$_2$H$_2$ cyclotrimcrimerization reaction has been shown to be structure sensitive on Pd with the Pd(100) surface showing a much lower yield of C$_6$H$_6$ than the Pd(111) surface [5,6]. With the larger Pd-Pd
separation distance for Pd films on Mo(100) factored in, it is then understandable that no C₆H₆ is formed on Pd films on Mo(100). It is somewhat surprising that no C₂H₄ is formed since some hydrogenation should occur.

The cyclotrimerization of acetylene to benzene has also been studied on Pd films on Au(111) [8]. Following saturation C₂H₂ exposure on an unannealed Pd monolayer on Au(111) at 170 K a single benzene desorption peak was observed at about 500 K. Increasing the Pd film thickness to 2 layers caused an increase in the amount of benzene desorption from this state. On a 3 monolayer thick Pd film the low temperature benzene desorption state at 250 K was visible. In addition a new state at approximately 410 K was observed at this thickness. This new state was associated with surface roughness since the films were unannealed. Increasing the Pd film thickness further caused a decrease in the amount of benzene desorbing and caused the peak at 410 K to disappear. The effect of annealing temperature on the reactivity of the Pd monolayer was also investigated. Annealing a Pd monolayer to 300 K followed by saturation C₂H₂ exposure resulted in a benzene desorption spectrum which greatly resembled desorption of reactively-formed benzene from bulk Pd(111). This was attributed to a higher degree of perfection in the Pd monolayer structure. Increased annealing temperatures caused an increase in the amount of benzene desorption from the low temperature desorption state and a decrease in the amount of benzene desorption from the high temperature desorption state. This was attributed to alloy formation between Pd and Au causing a decrease in the Pd ensembles needed to form a flat lying benzene.

Comparison with the present result is complicated by the different Pd film preparation procedures and the low temperature alloy formation for Pd/Au(111). However, the Pd monolayer on Au(111) clearly resembles bulk Pd(111) to a much greater extent than the Pd monolayer on Ta(110). This is due to the minimal
electronic perturbation caused by the Au substrate on the Pd layer. Recent photoemission work suggests that the surface valence d band for the Pd monolayer on Au(111) is somewhat more narrow than bulk Pd, but is not full and is not shifted towards higher binding energy to the same extent as seen for the Pd monolayer on Ta(110) [11]. Chemisorption studies of H₂ and CO also show the Pd monolayer on Au(111) to have only slightly perturbed chemisorption properties [11]. Thus, it appears that the effects observed for the Pd monolayer on Au(111) are due mainly to structural features of the film while for the Pd monolayer on Ta(110) the effect is due to the altered electronic structure.

Benzene chemisorption is also altered on the thin Pd films on Ta(110). Based on the results of Redhead analysis [10] and assuming benzene adsorption is not an activated process, benzene is bound to the θ_Pd = 1 film 6 kcal/mole less strongly than it is on the thick (θ_Pd = 5) Pd films or bulk Pd(111) [4,12]. Additionally, the propensity for reversible adsorption is greatly increased on the θ_Pd = 1 film. It appears that on the Pd monolayer much more benzene is able to pack on the surface. We propose this is due to the ability to form weakly bound species as evidenced by the chemisorption state which extends to temperatures as low as 200 K. The θ_Pd = 5 film resembles bulk Pd with respect to benzene chemisorption.

9.5 Summary

Ultrathin Pd films deposited on Ta(110) have altered chemisorption properties for C₂H₂ and C₆H₆ when compared to bulk Pd(111). The propensity for reversible adsorption is greatly increased on the θ_Pd = 1 film for both molecules. The cyclotrimerization of C₂H₂ to form C₆H₆ is found to occur on the θ_Pd = 1 film and the reactively-formed C₆H₆ desorbs from a single state at 400 K. In contrast, the same reaction on Pd(111) results in C₆H₆ desorption at 250 and 500 K. The different desorption temperature for reactively-formed C₆H₆ on the θ_Pd = 1 film is
attributed to a more weakly bound flat lying benzene species. This is consistent with TPD spectra of C₆H₆ following C₆H₆ exposures on a θₚd = 1 film, which also show C₆H₆ desorption at 400 K. Pd films two to three monolayers thick have some characteristics of the θₚd = 1 film as well as some characteristics of bulk Pd(111) while thicker (θₚd = 5) Pd films in general resemble bulk Pd(111).
REFERENCES FOR CHAPTER IX


CHAPTER X

CONCLUSIONS

The chemisorption properties of ultrathin Pd films deposited on Mo(100) and Ta(110) have been thoroughly investigated. The results demonstrate that the chemisorption properties of Pd are greatly altered from those observed on bulk Pd surfaces by depositing Pd on Mo or Ta. This is due mainly to the altered electronic structure of the Pd films rather than changes in the physical structure of the surface. In many respects the Pd monolayer has a chemical reactivity which approaches that of Ag. This is evidenced by the reduced molecule-surface bond strengths for CO, C$_2$H$_4$, C$_6$H$_6$, and hydrogen. Additionally, the propensity for reversible adsorption is increased for C$_2$H$_4$, C$_2$H$_2$, and C$_6$H$_6$ on the Pd monolayer film. NO adsorbs molecularly on the Pd monolayer on Ta(110) at 95 K and upon heating the surface desorption and dissociation compete to remove NO from the surface. Desorption products following NO exposures on the Pd monolayer on Ta(110) include NO, N$_2$O, and N$_2$. These desorption products are also observed to desorb from Ag(111) following NO exposures.

There is some ability to "tune" the chemistry of the surface by controlling the Pd film thickness. The molecule-surface bond strengths become larger as the Pd film becomes thicker than one monolayer. For Pd films deposited on Ta(110), a Pd film thickness of $\theta_{\text{Pd}} = 5$ is required to observe chemisorption properties similar to bulk Pd. Slightly thicker films are required for Pd films on Mo(100).

Further studies of ultrathin metal films deposited on dissimilar metals will help elucidate the origins of the improved performance of bimetallic catalysts over
their single metal counterparts. A logical extension of the present work is to perform similar studies with Pt films deposited on Ta(110). The growth and structure of Pt overlayers on Nb(110) appear to be quite similar to results for Pd on Nb(110) and Ta(110) [1]. Because of the similar lattice constants of Nb and Ta the growth and structure of Pt films on Ta(110) would likely also be similar. Photoemission results for a Pt monolayer on Nb(110) show a reduced density of states at the Fermi level and also indicate a lack of CO adsorption at room temperature, which is also analogous to the Pd/Nb(110) and Pd/Ta(110) systems. In contrast, the H\textsubscript{2} chemisorption properties of Pt films on Nb are quite different from those of Pd films [2].

Another intriguing extension of the current work would be to study the chemisorption properties of Pd and Pt films on Zr. The Pt-Zr system has already been shown to have interesting chemical properties and this can also be expected for Pd-Zr. Due to the difficulties of obtaining and maintaining a clean Zr surface this could possibly best be done by depositing thin films of Zr on W, annealing the Zr films, and then depositing Pd or Pt.

Finally, an investigation of the chemisorption properties of Ag films would be interesting. From an economic viewpoint it is desirable to increase the catalytic activity and selectivity of a relatively inexpensive metal to the point where it can replace a more expensive metal. Thus, it would be beneficial to effect a change in the electronic structure of Ag so that it would have the catalytic activity of Pt or Pd.

The growth and structure of Ag films deposited on Nb(110) have been studied with photoemission and LEED [3]. The LEED results show that Ag initially forms a commensurate monolayer but converts to a more close packed structure at a Ag coverage of about three monolayers. Photoemission results suggest only a small participation of the Ag d-band states in bonding with the Nb substrate. However,
only a small change in the surface electronic structure relative to bulk Ag may be needed to observe significant changes in the surface chemistry. This system would also serve as a distinctly different case when compared to the Pd/Nb and Pd/Ta systems where extensive bonding interactions are observed [4].
REFERENCES FOR CHAPTER X


G. Ertl and J. Kuppers, Low Energy Electrons and Surface Chemistry (Verlag-Chemie: Germany, 1974).


J. M. Heitzinger, A. Avoyan, and B. E. Koel, to be published.


A. Sellidj and B. E. Koel, to be published.


