INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road. Ann Arbor, MI 48106-1346 USA
313/761-4700     800/521-0600
Pt on graphite (0001): A model system for the study of physical and chemical properties of small metal islands

Eppell, Steven Joseph, Ph.D.

Case Western Reserve University, 1991

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106
PT ON GRAPHITE (0001)  
A MODEL SYSTEM FOR THE STUDY OF  
PHYSICAL AND CHEMICAL PROPERTIES OF SMALL METAL ISLANDS  

by  

STEVEN JOSEPH EPPELL  

Submitted in partial fulfillment of the requirements  
for the Degree of Doctor of Philosophy  

Thesis Advisor: Gary S. Chottiner  

Department of Physics  
CASE WESTERN RESERVE UNIVERSITY  
May 1991
CASE WESTERN RESERVE UNIVERSITY

GRADUATE STUDIES

We hereby approve the thesis of

Jane Epple

candidate for the Ph.D.
degree.*

Signed: [Signature]
(Chairman)

Date 4/23/9

*We also certify that written approval has been obtained for any proprietary material contained therein.
PT ON GRAPHITE (0001)
A MODEL SYSTEM FOR THE STUDY OF
PHYSICAL AND CHEMICAL PROPERTIES OF SMALL METAL ISLANDS

Abstract
by
STEVEN JOSEPH EPPELL

In order to aid in the search for fundamental understanding of the particle size effect in catalysis, a model system has been developed. The system consists of Pt vapor deposited onto the basal plane of highly oriented pyrolytic graphite, HOPG(bp). The electronic structure of Pt/HOPG(bp) has been probed with X-ray photoemission spectroscopy. It was found that there is a small decrease in the Pt 4f binding energy with Pt coverage (∼0.1eV in going from a 1% to a 50% monolayer coverage surface). There is a further decrease in binding energy of ∼0.1eV after the surface has been heated to ∼1000K. The morphology of the Pt islands has been studied with an ambient scanning tunneling microscope, STM. STM shows that Pt deposited on a 300K HOPG(bp) surface forms islands that are ∼5nm across and ∼0.4nm high. The height of the islands is insensitive to the Pt coverage between 1% and 50% of a monolayer. Heating the surface causes the island height to increase by a factor between 5 and 10 times. The gas phase chemical behavior of
Pt/HOPG(bp) has been probed with temperature programmed desorption, TPD, using $O_2$ and CO as adsorbates. The $O_2$ TPD peak increases in temperature by ~25K when the Pt/HOPG(bp) surface is pre-heated to ~1000K. The CO spectra show a broad series of peaks whose population shifts from the high temperature end to the low temperature end when the Pt/HOPG(bp) surface is pre-heated. Preliminary studies of the liquid phase chemical behavior of Pt/HOPG(bp) have been performed using both an in-situ and an ex-situ electrochemical cell. The in-situ work shows that an 80% Pt/HOPG(bp) surface displays a cyclic voltammogram in 0.1M KOH very similar to bulk Pt. A 5% Pt/HOPG(bp) surface was found to display stable behavior upon potential cycling in 0.1M KOH. The voltammogram had some but not all of the bulk Pt characteristics. The ex-situ work shows that 10% Pt/HOPG(bp) is capable of catalyzing CO oxidation. In addition, titration of the CO oxidation peak yields an active site density equal to one half the Pt coverage estimate by XPS.
To

Marvin, Adrienne, Paula, Beth and Lisa

Five of the best friends with whom a man could hope to walk through life.
PREFACE

Since the time of the Ancient Greeks, the spirit of reductionism has driven much of the science of the Western World. The basic premise of reductionism is that a profound understanding of a complex system can be obtained by dismantling that system into its most fundamental pieces. Implicit in this definition is that the relationships between the fundamental pieces must be understood. Modern high energy physicists have raced far beyond what is commonly termed "the atom" in their pursuit of the most fundamental units of matter. Our understanding of the relationships between fundamental pieces, however, has not kept pace. It is necessary to occasionally stop the process of disassembly and ponder the relationships between the pieces at hand.

For example, it is not well understood how assemblies of metal atoms conspire to give bulk properties. The theory of small metal particles is complicated because the number of atoms is too great to solve the system with ab-initio calculations (ex. Hartree-Fock) commonly used on assemblies of several atoms. Yet the system is too small and/or too poorly ordered to use the simplifying assumptions of periodic boundary conditions (ex. Bloch Waves) commonly applied to bulk systems. It is not surprising then, that the literature is filled with various theoretical approaches to these systems.¹⁻⁴ This leaves the scene ripe for an experimentalist to enter and clarify the situation by probing a model system with atomic scale tools. This idea is by no means a
new one as evidenced by the publication of many review articles on the subject.5-9

To strengthen the bond between this research and the society in which the research was taking place, it made sense to choose a model system bearing some resemblance to a current technology. Platinum is a metal of paramount importance in the areas of catalysis and alternative electric energy production. The role of Pt in these areas is as an active surface over which kinetically hindered reactions are made facile. Since Pt is a very expensive material, maximizing its dispersion (surface to volume ratio) is economically sensible. In addition, Pt has a relatively high density resulting in very heavy devices unless efforts are taken to maximize its dispersion. The usual approach is to deposit small clusters of Pt on an inexpensive, inert, low density substrate. (From here on, "cluster" will signify a gas phase particle and "island" will signify a supported particle.) High area carbon is often chosen as this substrate.

In experimenting with various systems, it was found that certain reactions displayed different behavior as a function of dispersion. It is often assumed that increasing dispersion implies decreasing island size; thus these changes in reaction rate with dispersion are commonly called particle size effects (PSE). Che and Bennett8 place these behaviors into two broad categories. First, the facile or structure-insensitive reactions which show no change in reaction rate with dispersion. Second, the demanding or structure-sensitive reactions which do show a change in reaction rate with dispersion. These demanding reactions are then divided
into three sub-categories. First, the antipathetic reactions in which the rate decreases with increasing dispersion. Second, the sympathetic reactions in which the rate increases with increasing dispersion. And third, sympathetic reactions in which the rate goes through a maximum and then decreases with increasing dispersion.

There is little disagreement in the literature that a PSE exists. The controversy arises when specific systems are analyzed and attempts are made to quantify the effect. Often the systems being analyzed are of direct industrial relevance but lack a high degree of definition with respect to surface characteristics, i.e. chemical composition and morphology.

The aim of this dissertation is to present a system in which this problem does not exist. The basal plane of highly oriented pyrolytic graphite, HOPG(bp), was chosen as a substrate because it at once provides a very well defined surface and a surface whose chemical composition, carbon, has direct technological significance. In addition, HOPG(bp) aids in the study of the strong metal support interaction (SMSI). This is a phenomenon in which an island's chemical activity is modified by the substrate on which it sits. It is often desirable to place an island on a substrate which will make a strong chemical bond with the island atoms; this will prevent the island material from being washed away with the reaction stream. However, if one is trying to examine the PSE, the SMSI interferes. HOPG(bp) is perhaps the least reactive conducting substrate available; thus it should present a very small SMSI. Platinum was chosen as the island material for the reasons
outlined above.

This system of platinum on graphite (Pt/HOPG(bp)) was studied with various techniques. The presentation of these studies will be as follows. First, the relevant literature on each technique as applied to Pt/HOPG(bp) is reviewed in Chapter I. Next, the details of the experimental equipment and procedures are enumerated in Chapter II. The results of the experiments along with a discussion of the results is given in Chapter III. Finally, a summary of the conclusions and brief discussion of future work is given in Chapter IV.
ACKNOWLEDGMENTS

First, I would like to thank my thesis advisor, Gary Chottiner, for providing a pleasant environment in which to work. 
His state of the art equipment, open door office, and nearly infinite patience helped me tremendously in my journey through graduate school. Dan Scherson is also deserving of prime acknowledgment for producing the seminal ideas that led to this thesis and for providing much of the driving force that kept the work moving.

I would also like to thank J. Gary Pruett for leading me by the hand into the amazing world of scanning tunneling microscopy. Many helpful discussions with Walter Lambrecht were instrumental in my understanding of the electronic structure of small metal particles. The electronic wizardry of Bob Leskovec saved me from apparently impossible situations several times. In addition, I thank all of the physics faculty at CWRU and Ernest Yeager who were quick to let me into their offices and their minds. The freedom with which ideas were discussed was truly outstanding.

It has been my pleasure to work with many brilliant students during my stay at CWRU. Among them, I would like to specially thank Pilar Herrera-Fierro, Fredy Zypman-Niechonski, and Kuilong Wang for providing friendships and insights that will last a lifetime.

Finally, singular thanks are due to my family and Amy Dodson for providing essential support during my graduate studies. I would not have finished the exercise as a sane man without them.
# TABLE OF CONTENTS

ABSTRACT .......................................................... ii

PREFACE .......................................................... v

ACKNOWLEDGMENTS ............................................... ix

LIST OF FIGURES .................................................. xii

LIST OF TABLES .................................................. xvi

CHAPTER I INTRODUCTION ......................................... 1

1 XPS ............................................................. 1
   1.1 Peak Shifts ............................................... 1
   1.2 Initial State Effects ................................... 2
   1.3 Final State Effects ..................................... 3
   1.4 Substrate Effects ....................................... 4
   1.5 Peak Shape ............................................... 5
      1.5.1 Peak Width ....................................... 5
      1.5.2 Peak Symmetry ..................................... 6

2 STM ............................................................ 7
   2.1 History of STM ......................................... 8
   2.2 Small Metal Particles .................................. 10
      2.2.1 Introduction ..................................... 10
      2.2.2 STM ............................................... 11

3 TPD ........................................................... 22

CHAPTER II EXPERIMENTAL ...................................... 34

1 SAMPLE PREPARATION .......................................... 34
   1.1 Substrate ............................................... 34
   1.2 Island Formation ...................................... 36

2 SAMPLE ANALYSIS ............................................. 38
   2.1 X-ray Photoelectron Spectroscopy ...................... 38
   2.2 Auger Electron Spectroscopy ........................... 42
   2.3 Thermal Desorption Spectroscopy ....................... 43
   2.4 Scanning Tunneling Microscopy ......................... 45
      2.4.1 Theory ........................................... 45
      2.4.2 Practical Considerations ......................... 51
   2.5 Cyclic Voltammetry ..................................... 54

CHAPTER III RESULTS AND DISCUSSION ...................... 58

1 XPS AND AES OF HOPG(bp) .................................... 58
   1.1 Survey Scans .......................................... 58
   1.2 Carbon 1s Peak ........................................ 61
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 HOPG(bp) Valence Band</td>
<td>63</td>
</tr>
<tr>
<td>1.4 AES</td>
<td>63</td>
</tr>
<tr>
<td>1.5 Oxygen</td>
<td>63</td>
</tr>
<tr>
<td>1.6 AES Anomalies</td>
<td>71</td>
</tr>
<tr>
<td>2 XPS of Pt/HOPG(bp)</td>
<td>73</td>
</tr>
<tr>
<td>2.1 Pt 4f Peak Shifts</td>
<td>74</td>
</tr>
<tr>
<td>2.2 Pt/HOPG(bp) Valence Band</td>
<td>80</td>
</tr>
<tr>
<td>2.3 Heated Pt/HOPG(bp)</td>
<td>86</td>
</tr>
<tr>
<td>2.4 Effect of Air Exposure on Pt/HOPG(bp)</td>
<td>88</td>
</tr>
<tr>
<td>3 STM</td>
<td>93</td>
</tr>
<tr>
<td>3.1 Graphite (0001)</td>
<td>94</td>
</tr>
<tr>
<td>3.1.1 Natural Graphite</td>
<td>94</td>
</tr>
<tr>
<td>3.1.2 HOPG ZYB</td>
<td>98</td>
</tr>
<tr>
<td>3.1.3 HOPG ZYC</td>
<td>103</td>
</tr>
<tr>
<td>3.1.4 OPG</td>
<td>103</td>
</tr>
<tr>
<td>3.2 Pt/HOPG(bp)</td>
<td>107</td>
</tr>
<tr>
<td>3.2.1 Pt/HOPG(bp) AT 300K</td>
<td>107</td>
</tr>
<tr>
<td>3.2.2 Heated Pt/HOPG(bp)</td>
<td>124</td>
</tr>
<tr>
<td>4 TPD</td>
<td>132</td>
</tr>
<tr>
<td>4.1 Oxygen</td>
<td>133</td>
</tr>
<tr>
<td>4.1.1 HOPG(bp)</td>
<td>133</td>
</tr>
<tr>
<td>4.1.2 Pt/HOPG(bp)</td>
<td>135</td>
</tr>
<tr>
<td>4.2 Carbon Monoxide</td>
<td>140</td>
</tr>
<tr>
<td>4.2.1 HOPG(bp)</td>
<td>141</td>
</tr>
<tr>
<td>4.2.2 Pt/HOPG(bp)</td>
<td>141</td>
</tr>
<tr>
<td>5 ELECTROCHEMISTRY</td>
<td>147</td>
</tr>
<tr>
<td>5.1 In-Situ Electrochemistry</td>
<td>147</td>
</tr>
<tr>
<td>5.2 Ex-situ Electrochemistry</td>
<td>154</td>
</tr>
<tr>
<td>CHAPTER IV</td>
<td>162</td>
</tr>
<tr>
<td>1 CONCLUSIONS</td>
<td>162</td>
</tr>
<tr>
<td>2 FUTURE WORK</td>
<td>165</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>167</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

CHAPTER I

Figure 3.1  Diagram of how the CO overlayer on Pt(111) compresses with increasing CO coverage.\textsuperscript{19} .... 29
Figure 3.2  Sticking coefficient of CO on Pt(111) as a function of CO coverage.\textsuperscript{19} .................. 29

CHAPTER II

Figure 2.1  "Schematic diagram of two successive layers of hexagonal graphite in (a) top view, and (b) side view. The unit cell is enclosed by a dotted line in (b)." (Text and figure from reference 19). .................. 50

CHAPTER III

Figure 1.1  XPS survey scan of bare HOPG. .................. 59
Figure 1.2  AES survey scan of bare HOPG. .................. 60
Figure 1.3  XPS spectra of the valence band regions of HOPG(bp), A, and alumina, B. .................. 65
Figure 1.4  AES survey scan of HOPG(bp) after heating the surface showing the lack of an O signal. ...... 66
Figure 1.5  XPS scan of the O region on a bare HOPG(bp) surface. The solid lines represent the best-fit curve and its constituents. .................. 68
Figure 1.6  AES survey scan of a clean HOPG(bp) surface showing "diffraction peaks" at low energy. ... 72
Figure 2.1  Pt 4f peak position vs. coverage showing no obvious trend. .................. 79
Figure 2.2  XPS spectra of the valence band region of Pt/HOPG(bp) at various coverages of Pt: (A) clean HOPG(bp), (B) 0.6% ML Pt, (C) 1.5% ML Pt. .................. 81

xii
Figure 2.3 XPS spectra of the valence band region of Pt/HOPG(bp) at various coverages of Pt: (A) 10% ML Pt, (B) 55% ML Pt, (C) Pt foil...... 82

Figure 2.4 Difference spectra of the XPS valence band region for low coverage Pt/HOPG(bp): (A) 0.6% ML Pt - clean HOPG(bp), (B) 1.5% ML Pt - clean HOPG(bp). 83

Figure 2.5(A) 0 region XPS spectrum of 5% ML Pt/HOPG(bp) after exposure to air. The spectrum is fit with three curves. 90

Figure 2.5(B) 0 region XPS spectrum of 5% ML Pt/HOPG(bp) after exposure to air. The spectrum is fit with four curves. 91

Figure 3.1(A) STM topograph of an Essex natural single crystal graphite (0001) surface. 95

Figure 3.1(B) 3D computer generated "photograph" of the topograph in Figure 3.1(A). 96

Figure 3.2 STM topograph of a freshly cleaved HOPG ZYB grade (0001) surface. 99

Figure 3.3 STM highly magnified current image of the HOPG ZYB (0001) surface. 102

Figure 3.4 STM topograph of an HOPG ZYC grade (0001) surface. 104

Figure 3.5 STM topograph of an ordinary pyrolytic graphite surface that had been prepared by polishing. 105

Figure 3.6(A) STM topograph of the masked portion of an HOPG(bp) surface that had a 10% ML Pt spot deposited elsewhere on the surface. 108

Figure 3.6(B) STM topograph of the 10% ML Pt spot alluded to in figure 3.6(A). 109

Figure 3.7(A) STM topograph of 1% ML Pt/HOPG(bp). 111

Figure 3.8(A) STM topograph of 18% ML Pt/HOPG(bp). 112

Figure 3.9 STM topograph of 40% ML Pt/HOPG(bp). 113

Figure 3.7(B) Central 100X100 nm² section of Figure 3.7(A). 114
Figure 3.8(B) Central 100X100 nm² section of Figure 3.8(A). .................................. 115

Figure 3.10 STM topograph of a Small island on a 10% ML Pt/HOPG(bp) surface. .......................... 117

Figure 3.11 STM current image of loosely associated features displaying units of atomic dimension on a 10% ML Pt/HOPG(bp) surface. ........................................... 118

Figure 3.12 Histogram of Pt island heights. ......................... 121

Figure 3.13 STM topograph of a 0.7% Pt/HOPG(bp) surface which had been heated to ~1000K in UHV. ......... 126

Figure 3.14 3D island on a heated 1.2% ML Pt/HOPG(bp) surface. .................................................. 129

Figure 3.15 Hexagonal 3D islands on a 0.7% ML Pt/HOPG(bp) surface. ............................................. 130

Figure 4.1 TPD spectrum of O₂ on: (A) bare HOPG(bp), (B) 10% ML Pt/HOPG(bp) as-deposited, (C) 10% Pt/HOPG(bp) after heating to 1000K. ............................... 134

Figure 4.2 Line drawing of a cuboctahedron and a truncated octahedron from reference 27. ...................... 138

Figure 4.3 TPD spectra for Cu on: (A) bare HOPG(bp), (B) 50% ML Pt/HOPG(bp) heated 3X to ~1000K, (C) 50% ML Pt/HOPG(bp) heated 2X to ~1000K, (D) 50% ML Pt/HOPG(bp) heated 1X to ~1000K. .................. 142

Figure 5.1 Cyclic voltammogram of Ni wire obtained using in-situ electrochemical cell. .......................... 150

Figure 5.2 Cyclic voltammogram of Pt wire in 0.1M KOH using the in-situ electrochemical cell. ........... 151

Figure 5.3 Cyclic voltammogram of 80% ML Pt/HOPG in 0.1M KOH using the in-situ electrochemical cell .... 153

Figure 5.4 Cyclic voltammogram of 5% Pt/HOPG(bp) in KOH using the in-situ electrochemical cell. ........ 155
Figure 5.5  Cyclic voltammogram of 10% Pt/HOPG(bp) in 0.1M HClO₄ using ex-situ electrochemical cell .... 157

Figure 5.6  Cyclic voltammogram of 11% Pt/HOPG(bp) in 0.1M HClO₄ that had been CO saturated and then flushed with N₂ using ex-situ electrochemical cell ................... 158

Figure 5.7  STM topograph of 18% ML Pt/HOPG(bp) after potential cycling between H₂ evolution and 900mV vs. SCE in N₂ saturated 0.1M HClO₄ .... 161
LIST OF TABLES

CHAPTER I

Table 3.1 TPD peak positions and FWHM from the literature for various Pt surfaces. ......................... 25
Table 3.2 TPD peak positions and FWHM from the literature for CO on various Pt surfaces. ................... 28

CHAPTER II

Table 2.1 XPS instrument resolution as a function of spot size and pass energy. ............................... 39
Table 2.2 Parameter table for XPS coverage estimates of Pt on HOPG(bp). ........................................ 40

CHAPTER III

TABLE 1.1 Diebold et al.'s plasmon losses from the graphite surface as determined by HREELS,23 ............. 62
TABLE 1.2 0 1S peaks seen on bare HOPG(bp). ....................... 67
TABLE 1.3 0 1S binding energies for a few molecules not listed in the PHI library. ............................ 69
TABLE 2.1 Means of the Pt 4f peak positions and FWHM. ... 73
TABLE 2.2 Statistical uncertainty in the means of the Pt 4f peak positions. ................................. 75
TABLE 2.3 Literature values for shifts in Pt 4f peak positions and FWHM with varying Pt coverage on various substrates.............................. 76
TABLE 2.4 Shifts in Pt 4f peak positions and FWHM for Pt/HOPG(bp). ............................................. 78
TABLE 2.5 Fermi edge and valence band centroid of Pt/HOPG(bp)................................................... 85
TABLE 2.6 Shifts in Pt 4f peak positions and FWHM of Pt/HOPG(bp) due to heating. ............................. 86
TABLE 2.7  O 1S peaks resulting from exposure of Pt/HOPG(bp) to air. .......................................... 92
TABLE 3.1  RMS roughness of various graphite surfaces as determined by STM. .............................. 106
TABLE 3.2  Mean height of Pt islands on HOPG(bp) as measured by STM. ..................................... 120
TABLE 3.3  Mean width of Pt islands on HOPG(bp) as measured by STM. ....................................... 122
TABLE 3.4  Parameters relevant to coverage estimate of Pt/HOPG(bp) using STM. ............................ 124
TABLE 4.1  TPD peak positions and FWHM from the literature for O₂ on various Pt surfaces. ............ 137
TABLE 4.3  Effect of heating on the TPD Peak positions for CO on Pt/HOPG(bp). ........................... 144
TABLE 4.4  TPD peak positions from the literature for CO on various Pt surfaces. Only CO coverages relevant to this work are included............. 145

xvii
CHAPTER I

INTRODUCTION

1 XPS

X-ray Photoelectron Spectroscopy (XPS) was used for three reasons. First, chemical composition of the surface region was assayed. Second, the Pt loading of the surface was determined. Third, electronic properties of the Pt islands were investigated by looking at core level and valence band peak positions and peak shapes. These types of experiments are numerous in the literature.\textsuperscript{1-8} As Mason points out in his 1983 review, carbon is the most used substrate in these studies.\textsuperscript{6} Outlined below is why it is expected that peak positions and shapes should change with island size.

1.1 PEAK SHIFTS

There are two groups of theories used to describe peak shifts with island size, the first refers to initial state effects and the second to final state effects. A spirited discussion of the relative importance of these effects can be found in the papers of Wertheim et al.\textsuperscript{3,7,9} and Bagus et al.\textsuperscript{4,10}
1.2 INITIAL STATE EFFECTS

Initial state effects refer to the interaction between electrons in an island before photoionization has occurred. To interpret peak shifts in XPS spectra, it is necessary to know what the interaction is between valence level electronic states and core level electronic states. Current understanding concerning these interactions is a bit confused. Below are presented two theories which predict opposite physical situations with respect to the electronic configuration of a given cluster but the same shift in binding energy as cluster size is varied.

The Renormalized-Atom Approach has been used to explain shifts in the XPS peaks of Pt. This theory predicts an increase in the charge residing in spatially localized ("d-orbital") valence states as a Pt cluster grows from one to many atoms. This causes the coulombic repulsion between valence and core electrons to increase with cluster size resulting in a decreased binding energy of both valence and core electrons.

A more rigorous self-consistent full band calculation has been done for bulk Pt showing that the charge residing in spatially localized valence states decreases with increasing cluster size. If it is assumed that the localized valence states are poor at screening the positive nuclear charge and that the delocalized sp-hybrid that the d-electronic charge moves into is good at screening; then it is expected that a decrease in localized charge will cause a decrease in binding energy. These screening assumptions are reasonable because d-states have zero amplitude at
the nucleus while s-states have an amplitude at the nucleus. Note that the screening mentioned here refers to screening of the nuclear charge in the neutral atom, not to an atom with charge +1. Thus, it is an initial state screening effect.

1.3 FINAL STATE EFFECTS

Final state effects are the result of not being able to screen the nuclear charge of the ionized island on a time scale short with respect to the photoionization event (\(-10^{-15}\)s).\(^1\) For heuristic purposes, the final state effects can be divided into two distinct processes: electrostatic charging and configuration screening.

A simple way to view electrostatic charging is to imagine a metal sphere suspended in vacuum. When the sphere is photoionized, the exiting photoelectron must escape the field presented by the positively charged sphere. This attractive field will raise the binding energy of the photoelectron.

Configuration screening can be explained with the following classical metaphor. Assume the electron that will be ejected by an incoming photon (the photoelectron) resides close to the nucleus. Because most of the other electrons in the cluster reside outside the photoelectron's orbit, Gauss' Law indicates that they are not able to screen the positive nuclear charge from the photoelectron. If it is assumed that the final state is the same as the initial state save only that a core hole is present, then the photoelectron must escape a relatively strong attractive potential. If, however, the other electrons are able to reconfigure themselves so as to screen the nuclear potential as the photoelectron leaves the
cluster, then the attractive potential is lessened. This will result in a shift to lower binding energy of the photoelectron.

In a strict quantum mechanical sense, the above explanations are not necessary. It is only important to calculate the matrix element for the initial and final states and then subtract the two energies to find the binding energy. This is a difficult calculation to carry out exactly for islands of many atoms on a substrate.

1.4 SUBSTRATE EFFECTS

Both the initial and final state effects are complicated by the presence of a substrate.\textsuperscript{3,4,6,7} If there is a chemical bond between island atoms and substrate atoms, then there can be screening of the nuclear potential of the island atoms by electrons from the substrate. It has been suggested that the Π state present on the surface of HOPG(bp) could form a delocalized metal-like bond with a metal cluster that was in close proximity to the surface. The resulting electronic configuration would allow electrons from the substrate to enhance screening effects during photoionization.\textsuperscript{13} This would diminish the shift in binding energy seen when the island grows from one to many atoms.
1.5 PEAK SHAPE

Changes in peak shape can be divided into two classes: changes in the width of the peak and changes in the symmetry of the peak. For the electronic states that lie near the Fermi Level, the width of their photoelectron peaks will increase as the number of atoms in the cluster increases. This is due to the increased number of interactions between electrons as the number of atoms in the cluster increases. As far as the core level electrons are concerned, at least two theories have been forwarded.

1.5.1 PEAK WIDTH

Parmigiani et. al suggest that atoms with different coordination will have different binding energies. A small island will have a broad distribution about the mean with respect to coordination, therefore it will show a broad XPS peak. A large island will have a sharp peak about the mean and thus display a narrow XPS peak.

Cheung suggests that plasmon damping is responsible for changes in peak width. In a small cluster, there is a coupling between plasmons and discrete electronic states which causes the plasmons to damp out. When calculating the line width of an XPS peak, it is necessary to multiply by the plasmon zero-loss-peak, $m\tau^{-1}$ ($m$ = average number of plasmons excited by the core hole, $\tau^{-1}$ for most metals, $\tau$ = characteristic plasmon coherence time). Cheung points out that $\tau$ is proportional to the cluster radius. So, as the cluster size increases, $m\tau^{-1}$ decreases thus the XPS peak
narrow. This can be understood with the following semi-classical model. Assume the plasmons are important in screening the final state core hole. If the plasmons have high mobility, they can easily screen the hole thereby lowering the final state energy. This results in a relatively stable, thus long lived final state. If, however, the plasmons are quickly damped, they will not be able to screen the final state core hole. This results in a high energy relatively short lived state. Application of the uncertainty relation $\Delta E \Delta t - \hbar$ then leads to the conclusion that plasmon damping causes increased line width. So, again, smaller clusters should have broader lines.

It should be noted that the above discussion applies to monodisperse assemblies of clusters. If the assembly is polydisperse, there will be several contributions to the photoelectron peak at slightly different energies. This will have the effect of broadening the width of the measured photoelectron peak but should not be misinterpreted as a broadening of the peak of any one cluster size.

1.5.2 Peak Symmetry

Changes in symmetry of a photoelectron peak can be attributed to formation of electron-hole pairs by the photoelectron as it exits the atom. For a single atom, it is not possible to form such a pair so no such scattering takes place and a symmetric XPS peak is measured. As bands begin to form and holes become possible, exiting photoelectrons can cause the formation of an electron-hole pair with a small loss in energy. This causes a high binding
energy tail to appear in the photoelectron spectrum resulting in an asymmetric peak. Thus it is expected that symmetry will decrease as island size increases. This is consistent with the more rigorous treatment reviewed by Cheung.\(^5\)

In summary, all the above theories agree that XPS peaks should change with cluster size in three ways. First, the peak positions should shift to lower binding energy with increasing cluster size. Second, the peak width should narrow with increasing cluster size. Third, the peak shape should shift from being symmetric about the peak mean to being asymmetric with a high binding energy tail as cluster size is increased. The size of these shifts (0.1eV-1eV) will be dealt with in Chapter III.

2 STM

After depositing Pt on the HOPG(bp) surface and investigating it with XPS, the surfaces were transferred through air to an ambient Scanning Tunneling Microscope (STM). (STM will be used to abbreviate both scanning tunneling microscope and scanning tunneling microscopy.) This technique was used to obtain morphological information about the surface: HOPG(bp) defects, Pt island height, Pt island lateral dimensions, and density of Pt islands on the surface. This section will give a brief history of the technique followed by a discussion of the few authors who have looked at small metal islands on HOPG(bp). A rudimentary discussion of the theory of operation of the STM can be found in
Chapter II.

2.1 HISTORY OF STM

In 1965 Russell Young at the National Bureau of Standards built a machine that he called "The Ultramicrometer."\(^1\) This device measured the distance between a sharp tungsten tip and a tantalum ribbon. A high voltage was applied between the tip and the ribbon causing an emission current to flow. The distance between tip and ribbon was then varied while keeping the emission current constant. Using the Fowler-Nordheim theory,\(^2\) Young was able to translate measured tip-ribbon voltages into tip-ribbon displacements. He was able to maintain separations of ~10nm quite reproducibly. Young foreshadowed the invention of the STM twice in this early work writing, "A more sensitive but much more limited device would apply a fixed emitter anode voltage and measure the dependence of emission current on electrode spacing. Such a device has been described by Trolan in the form of a transducer which converts mechanical motion to a change in electrical current.\(^3\)" Later in the paper he conjectures, "In the case of surface profile measurements ... a servo system employing the electrical information from the instrument might be used to scan and record the full detailed contour of a complex surface with extremely high vertical resolution, and with horizontal resolutions of the order of the emitter radius."

About five years later, Young, Ward and Scire measured for the first time metal-vacuum-metal tunneling between a W tip and a Pt surface using the type of field emitter device described above.\(^4\)
The tip in this work was supported on a triplet of orthogonal piezo drives used to measure surface profiles as outlined in Young's earlier paper. This new device was coined "The Topografiner." Young et al.'s interest in this work was in seeing the transition from tunneling to field emission. It would appear that the only crucial difference between The Topografiner and the STM was in measuring the current between tip and sample instead of the voltage. The current is exponentially dependent on tip-surface distance while the voltage is merely linearly dependent.

Ten years after the work of Young et al., Binnig, Rohrer, Gerber, and Weibel reproduced Young's W tip/Pt surface tunneling result. They obtained a stability of the tunneling gap of 0.02nm, approximately ten times better than that reported by Young et al. The authors postulate that this was probably the result of improved vibration isolation. The following year, 1982, Binnig et al. published the article "Surface Studies by Scanning Tunneling Microscopy" in Physical Review Letters. In this seminal work, images of monoatomic steps and surface reconstructions of CaIrSn₄(110) and Au(110) were shown. The scanning tunneling microscope was born and the world of surface science has not been the same since then.

In less than ten years since its introduction to the scientific community, STM has been used to address a host of problems, among them: the 7X7 reconstruction of Si(111), the origin of enhancement in surface enhanced Raman spectroscopy, the imaging of native DNA, the surface reconstruction of Pt(100) upon heating, the reconstruction of Pt(110) upon CO
adsorption,\textsuperscript{15,16} nucleation and growth processes,\textsuperscript{17} underpotential deposition of metals,\textsuperscript{18,19} and the study of small metal particles.\textsuperscript{21-25} Five international conferences have been held on STM, three having published proceedings.\textsuperscript{26-28} and a few reviews of the technique have been published.\textsuperscript{29-32}

2.2 SMALL METAL PARTICLES

2.2.1 INTRODUCTION

Before reviewing the literature on STM of small metal particles, a brief discussion of the paper "Adsorption and Desorption Kinetics of Cu and Au on graphite (0001)" by Arthur and Cho will be given.\textsuperscript{33} This interesting paper presents the results of experiments in which metals were vapor deposited on graphite (0001) and then removed by heating the graphite crystal. Metal atoms were detected leaving the surface by mass spectrometry. Using only this thermal desorption technique along with a mixture of theories\textsuperscript{34-36} and some original theory of their own, Arthur and Cho deduce a picture of what happens when single metal atoms are incident upon the graphite basal plane. This picture corresponds well with what is seen using STM.

Arthur and Cho find that both Cu and Au atoms impinge on the surface and are adsorbed with an accommodation coefficient of 0.8\textsuperscript{37} or 0.9. With the graphite at 300K, the atoms have an average surface residence time of less than 10\textsuperscript{-2}s and move across the surface with a speed of \textsuperscript{-2}cm/s. If 1/2 order kinetics is assumed along with a pre-exponential factor of 10\textsuperscript{13}sec\textsuperscript{-1}, a binding
energy of 0.65eV is calculated. In terms of surface diffusion barriers, work by Gomer et al. is cited.\textsuperscript{37,38} These authors find that for oxygen physisorbed on oxygen-covered tungsten, the surface velocity is also $\sim 10^{-2}\text{cm/s}$. In addition, they calculate that this corresponds to a barrier to surface diffusion of 0.04eV. This means that metal monomers on graphite (0001) can be modeled as a two-dimensional gas. After diffusing about on the graphite surface, a metal atom will desorb at a coverage dependent rate. Arthur and Cho find that the condensation coefficient is $<0.05$ for the clean graphite (0001) surface and increases to 1 at an unspecified coverage.

The best fit to Arthur and Cho’s data is found using a two-dimensional island nucleation and growth model. The authors thus conclude that, "...the formation and growth of two-dimensional nuclei (occurs) from a mobile surface atom population which is only weakly held by the substrate."\textsuperscript{54}

2.2.2 STM

Binnig and Rohrer claim to have observed Au particles before they found the Si(111)7X7 structure.\textsuperscript{30} This would make them the first to have imaged small metal particles; they did not publish these results. In 1986 Abraham et al. published the first images of small metal particles (Ag and Au) supported on graphite.\textsuperscript{20} The early work on STM of small metal islands from John Clarke’s group at The University of California, Berkeley is fascinating. In a series of three papers which culminate in Eric Ganz’s thesis, images displaying atomic resolution of supported metal clusters are
presented and interpreted. As with any pioneering work, a few mistakes were made along the way. Presented below is a critical review of these early papers. There is absolutely no intention of belittling the importance or overall correctness of the work.

Abraham et al. prepared their islands by vapor deposition onto a freshly cleaved HOPG(bp) substrate held at room temperature. The silver was deposited through 2.2 Torr of Ar. According to Granquist and Buhrmann, this should give a log-normal distribution of particles incident on the HOPG(bp) with mean size between 2 and 20 nm. The gold was vapor deposited in high vacuum. The amount of material deposited was monitored using a quartz crystal microbalance. No mention was made of any calibration procedure that may have been used. This is important since the sticking coefficients for Ag or Au on HOPG(bp) are likely to be much lower than the coefficients for the same metals on a metal covered quartz crystal. In any event, the authors report depositing 0.3nm of Ag and make no mention of the amount of Au deposited. Most of the images collected in this work were obtained with tunneling currents of several nA. It has been shown that when imaging HOPG(bp) in air, tunneling currents >2nA usually indicate that the tip is deforming the surface.\(^{23}\) \(^{(\text{p. 70})}\)

Abraham et al. show two examples of the many Ag islands they observed in their early work.\(^{20}\) The first is an island with lateral dimensions of ~35 nm and a height of ~3 nm. The image was collected in the topographic mode (constant current). The island has a segmented toroidal appearance displaying several shallow drops in height about its perimeter and a sharp drop in height in
the center. The authors claim that this is the result of the large island being an aggregate of several smaller islands 3-10 nm in width. They further suggest that "the presence and shape of the substructures suggest that the large cluster was formed by the coalescence of small mobile clusters after deposition, rather than in the beam prior to deposition."p.853 The only evidence offered in proof of this claim is the final structure of the island itself.

The second example of the Ag/HOPG(bp) surface is of a much smaller island collected in the current imaging mode. Here there appears to be a small string of ~5 Ag dimers that is 0.5nm wide and 1.4nm long. The atoms within each dimer are not resolved and the authors mention that they may be monomers that appear wider than expected for a single Ag atom. Over a period of 20 minutes, it appears that several more atoms diffuse into the region and associate with the island. The authors point out that "...the dimers are roughly commensurate with the graphite lattice, suggesting that the substrate-cluster interaction is by no means negligible."(p.854) It is interesting to note that this island of <20 atoms stayed fixed over a period of more than 30 minutes while the authors suggest that the first example of a larger island was formed by islands containing >100 atoms moving over the HOPG(bp) surface.

The Au/HOPG(bp) results reported are very preliminary in nature. The Au was vapor deposited through high vacuum (10^-6 Torr); no Ar was present. The authors cite Venables et al. in saying that this produces Au monomers incident on the surface.40 They found clean regions of HOPG(bp) adjacent to regions with
islands of "very large size."\(^{\text{p.854}}\) At the boundaries of these regions they occasionally found small islands. One of these islands is presented in the paper. It contains, "perhaps six or seven atoms with an average spacing of about 3\(\text{Å}.\)"\(^{\text{p.855}}\) The description of this surface is very similar to surfaces examined in this thesis which contained \(\sim50\%\) of a monolayer of Pt.

Finally, the authors caution against overinterpreting these images. They point out that airborne contaminants, particularly water and oxygen, may interact with the surface profoundly affecting the behavior of the adsorbed metal atoms. Some insight into this problem will be given in the XPS and TPD results and discussion sections of this thesis.

In 1987 at the 2\(^{\text{nd}}\) International conference on scanning Tunneling Microscopy, Ganz et al. presented the first STM images of small metal islands on HOPG(bp) where the islands were produced and imaged in UHV.\(^{21}\) In addition to Ag and Au, Al islands were also investigated in this paper. The authors say they used HOPG as a support for a few reasons, among them that it is easily cleaved giving atomically flat planes over many square microns. They site Ignatiev and Wu in justification of this claim.\(^{41}\) This reference, however, concerns natural graphite crystals, not man made graphite. In addition, it says that the only way to get nearly defect free basal planes over many microns is to cleave the crystal with a dry nitrogen jet. They specifically say that cleavage with Scotch\textsuperscript{TM} tape or a razor blade does not give defect free surfaces. It is found that of the ABAB... stack that makes up the bulk crystal, both A and B planes are exposed when cleavage is accomplished with
one of the latter two methods. Ganz et al. do not mention in any of their papers how they cleaved their graphite. However, most STM users take advantage of the ease presented by the adhesive tape cleaving procedure. Ganz et al. did examine areas ~1 \mu m^2 in size and found only a perfect graphite lattice with no observable contamination over the entire area. This thesis will present STM images of the same type of substrate used by Ganz et al. and show at what length scale defects in the HOPG(bp) do appear. In addition, LEED and XPS results will be given which indicate that the surface is not defect free.

In this second paper, Ganz et al. produced their islands using vapor deposition monitored by a quartz crystal microbalance. Here they do make note of the fact that Arthur and Cho have shown that the sticking coefficient for metals on HOPG(bp) may be <0.1.\cite{33} After deposition of ~1\% of a monolayer of Ag (as measured by the balance), they surveyed an area of 1x10^6 nm^2 and found 1.2x10^3 nm^2 covered with Ag adatoms. Thus the STM coverage estimate agrees with the microbalance estimate. This type of experiment was not repeated many times.\cite{42}

Typical tunneling conditions in this work were 5 mV bias voltage and 10nA tunneling current. Ganz later showed that there may be significant deformation of the graphite surface at this tunneling current even in vacuum if the surface has not been heated to remove contaminants.\cite{23} (p. 75) He also showed that tip contamination causes surface deformation. To avoid this problem, tips in his UHV experiments were cleaned by field emission to a clean Si surface before imaging began. In this work,\cite{21} Ganz et al.
found that currents <10nA produced noisy images while currents >10nA caused the tip to break up the islands and to perform in a generally unstable fashion. The authors were able to image monomers, collections of monomers, a dimer and a trimer. Monomers were only found within 1nm of a larger cluster. No isolated atom was ever found over a hole site. It is pointed out that this is in distinct contrast to the adsorption of noble gases physisorbed at low coverages. The noble gases form a regular net with atoms located above the hole sites. Ganz et al. reference Gooding et al.\textsuperscript{43} to show that application of the Lennard-Jones potential predicts that adatoms will sink down into the hole sites. However, the paper by Gooding et al. states that the registered phase has a binding energy of -41.5meV/atom; thus it is clear that the surface must be cooled much lower than room temperature in order to obtain a regular net. As suggested by Arthur and Cho,\textsuperscript{33} metal atoms on graphite (0001) at room temperature behave like a two dimensional gas. This indicates that comparison of metal atoms on a room temperature surface with noble gases on a cooled surface is probably inappropriate. It might be expected that the metal atoms would appear at hole sites if the surface was cooled during metal deposition. Finally, taking into account the facts that metal atoms appear on $\beta$-sites and $\beta$-$\beta$ bridge sites and that they are stable for periods of seconds to many minutes the authors conclude that, "for monomers and very small clusters, the effects of substrate-adsorbate interaction are important even for the relatively inert graphite substrate."\textsuperscript{21 (p.423)}
In 1989 Ganz et al. published a comprehensive review of their STM work up to that time. This paper contains images of Cu adatoms, thus completing the Ag Cu Au transition metal series of the periodic table. Also included are the first measurements of surface diffusion barriers by STM. There is presented a series of images ranging from monomers to two dimensional islands to three dimensional islands. The monomers were often visible during only one scan (~1s). After extensive searching, some monomers were found that were stable for several seconds. Consistent with their previous experience, Ganz et al. find monomers only within 1nm of larger islands.

Also presented are images of Ag and Au dimers in which the individual atoms are distinguishable. The authors point out that this is unexpected. The dimer bond should have high electronic density and thus present a high tunneling current. It is suggested that "perhaps charge transfer to the substrate (or some other metal-carbon interaction) weakens the dimer bond and localizes the electrons."^{22} (p39) A linear Ag trimer and a triangular Al trimer were imaged. The authors cite that the 0.25nm ±0.02nm spacing of the atoms in the Al trimer is in good agreement with Upton's theoretical result ~0.26nm.^{44} They do not discuss the fact that both Ag and Al have the same 0.25nm spacing and that this is very near the 0.246nm periodicity of the graphite lattice.

The effect of the tunneling current set point on the apparent size of an imaged island is investigated using a Ag dimer and a Ag trimer and varying the set point from 4 nA to 17 nA. In the current imaging mode, decreasing the tunneling current set point
causes the island size to decrease. In the topographic mode, the converse is true. This is explained as follows. Decreasing the tunneling current causes the tip to move away from the surface. The current density of an island decreases as distance from the surface increases. Thus, as the tunneling current set point is decreased and the tip moves away from the surface, the current density from the island results in a smaller image. The topographic mode, however, is not based on a measurement of current density at a fixed height. Instead, it relies on a measurement of the height at which current density remains constant. The S shell that forms the valence level of the Ag island has a spherical shape. Thus, as the tip is moved further from the island, the size of the contour of constant current density will increase with tip-surface distance.

Ganz et al. attempted to measure the size of the adatoms used in the tunneling current study described above. However, when looking to the HOPG substrate for a standard in length in the z-direction, they find that the graphite corrugation is 0.25±0.28nm, ~3X larger than it should be. This indicates that the surface was being deformed by the tip while collecting these images. They find a monotonic increase in atom size with decrease in set point current: island volume (4, 9, 10, 12, 45)Å³ at set point current (17, 15, 12.5, 7.5, 5)nA. Their conclusion is "that one cannot make useful measurements of the sizes of atoms in STM images without extensive knowledge of the tunneling conditions and a detailed theoretical model."22 (p.44) The most recent paper on this subject is that of Eigler et al.45 These authors combine the
calculations for atom on metal density of states by Lang with
the STM theory of Tersoff and Hamann and obtain quantitative
agreement with the image of a single Xe atom physisorbed on Ni(110)
at 4K.

Ganz et al. observed many two dimensional islands on the
graphite surface. Often these islands displayed a roughly
rectangular perimeter; the perimeter was not smooth. It is pointed
out that Drechsler et al. measured the self diffusion of large Au
islands on graphite. They assumed the diffusion constant has the
form $D=D_0 \exp(-\Delta E_s/k_B T)$ and found a barrier for self-diffusion, $\Delta E_s$,
of 0.34eV/atom with $D_0=5 \times 10^{-9} \text{cm}^2/\text{s}$. Assuming $k_B T=0.025 \text{eV}$ and using
the result from a 2D random walk analysis that $D=1/4 \lambda^2 v$ where $\lambda$ is
the hopping length and $v$ is the attempt frequency, it is found that
$v \approx 60 \text{sec}^{-1}$; thus, several minutes should be sufficient to smooth out
the rough edges of the clusters. Ganz et al. conclude that "self-
diffusion at the cluster edge is not important, presumably because
the substrate interaction pins the atoms, maintaining


The atoms within two dimensional Au islands are found to
arrange themselves in both linear and buckled chains. The lattice
spacings for two islands are given as (0.247±0.006 nm)X(0.39±0.01
nm) and (2.35±0.01 nm)X(3.5±0.01 nm). The nearest neighbor
spacings are found to be 10% to 15% smaller than predicted by the
theoretical calculations of Tomanek et al. The contraction in
bond length is tentatively attributed to a substrate interaction.

Unlike the two dimensional islands, three dimensional metal
islands have been studied extensively in the literature. Ganz
et al. found Cu islands that were three dimensional on HOPG(bp). They do not specify any special procedure used to obtain the three dimensional islands. No atomic structure is visible within these islands. The general outline of the one Cu island on an HOPG(bp) terrace shown in their paper is that of a rectangular solid with dimensions 16nm X 7nm X 2.5nm. The sides of the rectangle are not smooth but instead consist of many adjacent lobes of various sizes. Another set of three dimensional Cu islands adsorbed at what the authors refer to ambiguously as both a grain boundary and a step edge is shown. There is no proof given that the ledge with which the Cu islands are associated is simply a step or is indeed a grain boundary with a different orientation of the graphite atoms on either side of the ledge. In any event, there is a 1nm rise in going from the bottom of the ledge to the top; it was at least 500nm in length and in following along the step it was found to change its direction in increments of 120°. The islands associated with the ledge are roughly spherical in shape with diameters ranging from 2nm to 8nm (the mean diameter was 4.4nm). Only 25 islands were imaged along this step. The authors point out in their concluding remarks that increased statistics would give a better picture of the surface. This thesis will present such statistics.

The metals studied by the authors above are interesting in that Ag→Cu→Au represents an s-transition metal series, and Al is an example of a p-metal. However, none of them are particularly interesting from a catalysis point of view in general or an energy conversion point of view in particular. For this reason, it would
be very interesting to look at one of the d-transition metals. This thesis presents the results of such an experiment using Pt as the sample d-transition metal.

There have been a few previous reports of STM of Pt islands on various substrates (mica and glassy carbon).\textsuperscript{63-66} The Pt was RF sputter deposited,\textsuperscript{64,66} electrochemically deposited,\textsuperscript{65} vapor deposited\textsuperscript{63} and in one case, Pt crystallites were made on a bulk Pt surface by electrochemical potential cycling.\textsuperscript{63} Vazquez et al. were the first to examine vapor deposited Pt with STM.\textsuperscript{63} They deposited a 5nm film on mica and found what they describe as columnar growth of the Pt. Only one line scan image is presented and it shows what appear to be chains of Pt about 2nm high and 4nm X 10nm in lateral dimension. The chains are all oriented in roughly the same direction. Fan and Bard\textsuperscript{64} were also among the first to image Pt on mica. They RF sputter deposited \textgreek{g}1um Pt on the mica and imaged what they describe as a very smooth surface. The line scan images they published show almost no corrugation in the film. Shimazu et al.\textsuperscript{65} electrochemically deposited Pt onto glassy carbon. The amount of Pt deposited was 15.1 \textmu g/cm\textsuperscript{2} (this corresponds to \textgreek{g}2.8 ML). The authors find islands 30\textgreek{g}60 nm in lateral dimension with heights of \textgreek{g}10nm. The general shape of the islands imaged by STM was spherical. These authors compare the STM results with SEM results. The SEM showed that a 15.1 \textmu g/cm\textsuperscript{2} loading produced islands that were rectangular in cross section and \textgreek{g}2.3 nm in size. The authors suggest that the discrepancy between STM and SEM is due to tip shape effects inherent to STM. This is possible, though the later images of three dimensional Cu islands
by Ganz et al.\textsuperscript{22} show that the STM is capable of imaging rectangular solids. Scott et al.\textsuperscript{66} made more recent measurements of Pt RF sputter deposited on mica. These authors point out that to image an island on mica, one must first deposit a thin conducting film on the surface. Thus, the STM work of metals on mica is actually work of metals on a thin metal film. In any event, Scott et al. find images very similar to those of Shimazu et al. for film thicknesses between 4 nm and 20 nm. Their images of a 4 nm film do not look like the 5 nm film imaged by Vazquez et al.\textsuperscript{63} Scott et al. find that for films thicker than 20 nm, the images become much smoother and begin to look similar to those of Fan and Bard. The first report of STM images of Pt on HOPG(bp) along with the first images showing atomic resolution within small Pt islands was by Eppell et al.\textsuperscript{25} The results of this work are given in section 3.2 of Chapter III in this thesis.

3 TPD

After the morphological and electronic properties of a surface have been investigated, the next logical step is to examine the interaction of the surface with some simple molecules. Oxygen and carbon monoxide have been studied extensively on Pt surfaces since Langmuir's early work.\textsuperscript{1} These gases proved useful in this work for three reasons. One, they both chemisorb and desorb molecularly making the system relatively easy to analyze. Two, CO has been studied on Pt islands previously. Three, O\textsubscript{2} has states that desorb
below room temperature allowing for a probe of the islands that
does not require temperatures near the sintering point of Pt.
Below is a discussion of some of the vast literature germane to CO
and $O_2$ on platinum. It is intended to prepare the reader for the
comparison of Pt/HOPG(bp) to previously published results presented
in Chapter III.

Dioxygen has been shown to chemisorb and desorb below room
temperature when adsorbed on Pt foils\textsuperscript{2,3} Pt(111),\textsuperscript{4-8} Pt(110),\textsuperscript{9}
Pt(100)\textsuperscript{10} and various stepped Pt surfaces.\textsuperscript{11,12,13} First Langmuir\textsuperscript{1}
and much later Kneninger and Netzer\textsuperscript{14} discovered that results of $O_2$
studies are very sensitive to CO impurities. Molecularly adsorbed
$O_2$ is in an activated state and quickly reacts with gaseous CO to
form CO$_2$. On the other hand, CO is relatively inert when adsorbed
on Pt and acts as a poison to subsequent CO oxidation via a
competitive adsorption mechanism. This is an important
consideration for the surface scientist since CO is generally one
of the more plentiful gases in stainless steel ultra high vacuum
(UHV) chambers.

Using XPS, Luntz et al. showed that $O_2$ physisorbs on Pt(111)
at 25K.\textsuperscript{8} The predominant oxygen peak at this temperature is found
at 535.8eV which they attribute to a weakly bound (physisorbed)
state. Upon heating to 45K, this peak shifts to 530.8eV and above
150K the peak shifts again to 530.3eV. In what is probably the
most comprehensive piece of work of oxygen on platinum, John Gland
clarifies that the 45K-150K oxygen exists as a molecularly
chemisorbed species.\textsuperscript{11} After dosing the Pt with equal amounts of
$O_2^{32}$ and $O_2^{36}$, he found no mixing between the isotopes in the TPD
peak occurring near 150K. In addition, Gland and others\textsuperscript{5,6} used High Resolution Electron Energy Loss Spectroscopy (HREELS) to show that the oxygen is bound in a side-on, η\textsuperscript{2}, manner and exists in a peroxo-like, O\textsuperscript{2−} state.

It is useful to note that not all Pt surfaces show a molecularly desorbing state at 150K. There is quite a range of temperatures at which this peak occurs depending on the type of Pt surface. The peak temperatures for most of the low temperature desorption work reported in the literature are listed in Table 3.1. All peak positions and FWHM in this table and in Table 3.2 below were measured directly from the curves presented in the literature. No peak fitting is reflected in the data reported here.

All of the authors above find that not all the oxygen desorbs in the molecular state near 150K; there is a second peak around 700K. Gland's work does show isotopic mixing in this peak. In addition, HREELS data\textsuperscript{4} indicate a shift in the main loss peak from 870cm\textsuperscript{-1} (characteristic of the peroxo-like species) below 150K, to 490cm\textsuperscript{-1} (characteristic of the Pt-O stretch) above 300K. Finally, Low Energy Electron Diffraction (LEED) studies on O/Pt(111) show that above the 150K desorption peak, an ordered (2X2) overlayer pattern appears.\textsuperscript{11} This is consistent with atomically chemisorbed O atoms lying in 3-fold hollow sites on the Pt surface.

In summary, O\textsubscript{2} physisorsbs on Pt at 25K. It chemisorbs in a peroxo-like state around 45K. Most of this chemisorbed oxygen molecularly desorbs between 130K and 270K. The remaining oxygen dissociates into an atomically chemisorbed state which then desorbs around 700K.
Table 3.1

<table>
<thead>
<tr>
<th>Surface</th>
<th>Desorption Peak (K)</th>
<th>FWHM (K)</th>
<th>Heat Rate Rate (K/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(110)</td>
<td>244</td>
<td>51</td>
<td>NA</td>
<td>9</td>
</tr>
<tr>
<td>Pt(110)(1X2)</td>
<td>200,175</td>
<td>NA</td>
<td>NA</td>
<td>13</td>
</tr>
<tr>
<td>Pt foil</td>
<td>200</td>
<td>175</td>
<td>NA</td>
<td>2</td>
</tr>
<tr>
<td>Pt foil</td>
<td>187</td>
<td>67</td>
<td>NA</td>
<td>3</td>
</tr>
<tr>
<td>Pt filament</td>
<td>180</td>
<td>33</td>
<td>5.6</td>
<td>15</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>152</td>
<td>10</td>
<td>4.75</td>
<td>11</td>
</tr>
<tr>
<td>Pt(S)-12(111)X(111)</td>
<td>148</td>
<td>12</td>
<td>4.75</td>
<td>11</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>140</td>
<td>17</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>133</td>
<td>9</td>
<td>25</td>
<td>8</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>150</td>
<td>38</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td>Pt(321)</td>
<td>148</td>
<td>44</td>
<td>10</td>
<td>12</td>
</tr>
</tbody>
</table>

TPD peak positions and FWHM from the literature for various Pt surfaces.

There is TPD work in the literature using CO instead of O₂ that examines surfaces much more similar to the Pt/HOPG(bp) islands of this thesis than to a single crystal face.¹⁶⁻¹⁸ In particular, Altman and Gorte have looked at Pt vapor deposited on Al₂O₃.¹⁶,¹⁷ By using the area beneath the CO TPD curve as a measure of Pt surface area and a quartz crystal microbalance to measure Pt
volume, they calculate radii of their Pt islands. The details of these calculations are not presented in their papers, but the calculation can be done as follows:

1) Assume a distribution of uniform size islands.

2) Assume all islands are spheres. (This assumption is explicitly stated by Altman and Gorte)

3) Parameterize the problem as:

\[ A_{Pt} = \text{Area of a single Pt island} \]

\[ V_{Pt} = \text{Volume of a single Pt island} \]

\[ N = \text{Number of Pt islands on surface} \]

\[ r = \text{Radius of Pt island} \]

\[ \alpha = \text{Constant of proportionality relating the area under a TPD curve with the surface area (number of surface sites) of a Pt island} \]

\[ \beta = \text{Constant of proportionality relating a quartz crystal microbalance frequency shift (\(\Delta f\)) to the volume (total number of atoms) in a Pt island} \]

4) \[ A_{Pt} = 4\pi r^2 = \alpha(\text{area under TPD peak}) = \alpha(\text{TPD}) \]

5) \[ V_{Pt} = \frac{4}{3} \pi r^3 = \beta \Delta f \]

dividing 4 by 5

6) \[ \frac{A_{Pt}}{V_{Pt}} = \frac{3}{r} \]

solving for \(r\) and using the experimentally obtainable parameters

7) \[ r = \frac{3\beta \Delta f}{\alpha(\text{TPD})}. \]

For the purposes of brevity, all the Pt/CO results from the
literature will not be presented here. Instead, results from some of the larger laboratories along with those of Altman and Gorte are presented in Table 3.2.

In general, it is assumed that CO bonds to metals "through coupling of the $5\sigma$ orbital of CO to the sp bands of the metal and back-donation of metallic d electrons into the $2\Pi'$ orbitals."\(^{19}\) However, Ertl et al. point out that this does not seem to be the case with Pt where back donation from d orbitals is not as pronounced as in other group VIII metals.

In a relatively early paper, Ertl et al.\(^ {19}\) used LEED to show that on Pt(111) at 1L exposure, CO adsorbs in a $\sqrt{3}x\sqrt{3}$/R30° pattern. To obtain clearly defined LEED spots, it was necessary to cool the sample to 170K after dosing. If the sample was subsequently heated, the pattern became diffuse and completely disappeared by 350K but reversibly reappeared upon cooling. Increasing the dosage to 2L caused a change to a c4X2 pattern. Further increases in exposure cause this structure to compress, as shown in Figure 3.1. The c4X2 structure and its subsequent compressed forms did not display the order-disorder transition apparent at "low coverage." This was attributed to short range repulsive interactions which keep the CO molecules from making large displacements even at high temperatures.

Ertl et al. used TPD only on surfaces with CO coverages of <0.5 (the coverage limit for a room temperature surface). They found that the TPD peak positions were coverage dependent. In going from a coverage of 0.07 to 0.45 on a Pt(111) surface, a monotonic decrease in peak position from 470K to 415K was observed.
Table 3.2

<table>
<thead>
<tr>
<th>Surface</th>
<th>Peak (K) Mean</th>
<th>Peak (K) FWHM</th>
<th>Heat (K/s) Rate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>11Å Island</td>
<td>502</td>
<td>150</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>17Å Island</td>
<td>535</td>
<td>100</td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>35Å Island</td>
<td>470,510$^5$</td>
<td>120</td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>40Å Island</td>
<td>428,510</td>
<td>150</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>50Å Island</td>
<td>445</td>
<td>150</td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>70Å Island</td>
<td>398,488</td>
<td>180</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>Film</td>
<td>382,510</td>
<td>196</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>Film</td>
<td>420,510</td>
<td>7</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>415→495$^*$</td>
<td>112→52</td>
<td>15</td>
<td>19,20</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>523</td>
<td>106</td>
<td>4</td>
<td>21</td>
</tr>
<tr>
<td>Pt(321)</td>
<td>428,554</td>
<td>10</td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>552</td>
<td>86</td>
<td>50</td>
<td>23</td>
</tr>
</tbody>
</table>

$^*$ Values separated by an "→" indicate a range of desorption temperatures.

$^5$ Values separated by a ",," indicate a doublet in the TPD spectrum

TPD peak positions and FWHM from the literature for CO on various Pt surfaces.
Figure 3.1  Diagram of how the CO overlayer on Pt(111) compresses with increasing CO coverage.$^{19}$

Figure 3.2  Sticking coefficient of CO on Pt(111) as a function of CO coverage.$^{19}$
This shift is attributed to long-range repulsive interactions between the adsorbed CO molecules.

Finally, Ertl et al. measured the sticking coefficient as a function of coverage using a Kelvin probe calibrated with TPD and LEED results, Figure 3.2.

In another early but quite comprehensive work, McCabe and Schmidt studied CO adsorption on all three low index surfaces of Pt.\textsuperscript{23} In this work, curve fitting was attempted and wide peaks deconvolved into two or more narrower peaks. They found single asymmetric peaks with no shift in peak temperature up to coverages of 0.1 for the three low index planes indicating first order desorption kinetics. However, at higher coverages at least two states were present on each crystal face. In a later paper by Gorte and Schmidt,\textsuperscript{20} the contradictory result was found that Pt(111) shows a symmetric peak which shifts strongly with coverage. HREELS data from this paper shows that at low coverage CO is terminally bonded ($\nu = 2090\text{cm}^{-1}$) and at higher coverage a bridge bonded CO becomes possible ($\nu = 1860\text{cm}^{-1}$). McClelland et al.\textsuperscript{22} summarize that infra-red reflection spectroscopy, dynamic work function change measurements, and LEED all give results consistent with the HREELS data of Gorte and Schmidt.

McCabe and Schmidt point out that Pt(100) presents a particularly complicated spectrum. They attribute this to the surface reconstructing upon high enough exposure to CO. The clean Pt(100) shows a (5X1) reconstruction which reverts back to a (1X1) surface upon CO adsorption. There is a state that gives a peak at 560K which is coverage independent. This is attributed to a four
fold coordinated CO and is noted to be higher in binding energy than any of the Pt(111) or Pt(110) states. It is interesting to note that clean Pt(110) also shows a reconstructed surface. In this case, a (2×1) reconstruction is lifted upon adsorption of CO. However, this surface shows a fairly simple TPD spectrum containing only two peaks. Hofmann et al.²¹ confirm that the high temperature peak from Pt(110) (the only peak attainable at exposures below 2L) is no different on the (1×1) surface than it is on the (2×1).

McCabe and Schmidt also measured sticking coefficients by taking the slope of their coverage vs. exposure data. The shape of their sticking coefficient vs. coverage curves are very similar to that of Ertl et al. shown in Figure 3.2. The highest coefficient was obtained for Pt(110) and the lowest for Pt(100) with relative ratios of 1:1.4:2.7 for Pt(100), Pt(111) and Pt(110) respectively.

When the above authors found high temperature components to their TPD spectra, they were often attributed to desorption from kink sites. In an effort to examine these type of sites, McClellan et al.²² looked at CO on Pt(321). This surface is atomically rough having 40% of the surface atoms coordinatively unsaturated. In terms of the low index planes, Pt(321) is comprised of (111) terraces three atoms wide with steps that expose (100) sections two atoms wide and close packed (111) planes. This group finds no shift in peak temperatures with coverage. Only the 554K peak appears at low coverage and the 428K peak begins to grow around Θ=0.5. Their conclusions drawn from TPD and HREELS data indicate: at low coverage, CO adsorbs on the atomically rough step sites primarily in a terminal atop configuration but some bridge bonded
CO is also observed; at higher coverage, CO adsorbs on the Pt(111) terraces; the step site desorption peak is at 556K and the terrace site peak is at 436K; these states do not fill sequentially indicating limited CO mobility; none of the CO dissociates upon desorption.

Finally, a description of the TPD work done with CO on Pt islands is in order. Altman and Gorte originally studied Pt vapor deposited on an amorphous alumina support. The support was made in-situ by vapor depositing 500 nm of Al on a Ta foil and then oxidizing the deposited film at 800K in 1X10^-8 Torr oxygen. They reused these supports by Ar ion sputtering the Pt off to obtain a clean surface. As deposited Pt was found to grow in a layer by layer fashion. After depositing the Pt, small islands were obtained by heating the substrate to 700K. The size of the resulting islands was calculated as shown above. Altman and Gorte later extended their work to Pt on α-Al₂O₃ and found results nearly identical to those on the amorphous alumina.

At the smallest island size (1.1 nm), their TPD results show a broad peak at 502K. A peak around 380K grows as the island size increases. Altman and Gorte state that only "two desorption states at 400K and 510K are ... observed for any of the samples." They do not, however, present or even mention any peak fitting procedure that was performed. It was found that the two states filled sequentially. Expecting their smallest particles to behave like a rough surface, the authors compare their 510K peak to McClellan et al.'s 554K peak. It is interesting to note that even the 1.1 nm particles show sequential filling of the 400K state in contrast to
the non-sequential behavior of the bulk Pt(321) surface. The 400K state is associated with Pt(111) sites which is reasonable because this is the only low index face with such a low temperature desorption peak.

Immediately after depositing 2.5X10^{14} \text{atoms/cm}^2, the authors find a peak at 524K whose area is sufficient to account for 100% of the Pt being available for CO adsorption. The second TPD spectrum obtained on this surface shows a shift to 485K with a low temperature shoulder indicating the presence of the 400K species. There is also a 25% reduction in peak area. This change is attributed to formation of small 3-D islands through a process other than sintering. It is suggested that the temperature is too low and the island formation too fast to be explained by sintering. Instead, it is postulated that the as-deposited Pt is in an unstable 2-D state which is able to quickly aggregate to a more stable state when heated above 650K.

Finally, Altman and Gorte find no dissociation of CO upon desorption for any island size.
CHAPTER II
EXPERIMENTAL

This chapter will introduce the details of the experiments done in this work. The text is divided into three logical sections. A brief review of the substrate preparation technique is presented followed by an explanation of how Pt islands were formed then a description of the analytical techniques used.

1 SAMPLE PREPARATION

1.1 SUBSTRATE

All sample surfaces were prepared using Union Carbide highly oriented pyrolytic graphite (HOPG) crystals as the substrate. HOPG is a man made graphite crystal with a basal plane (bp) populated by a group of well aligned crystallites. As Arthur Moore explains in his comprehensive review,¹ the crystals are made with a two step procedure. First, a carbon containing gas is used to make a thick (several mm) carbon film on a substrate mounted in a hot furnace. Typical conditions are a pressure of 1-10 torr and a temperature of 2000-2200°C. If gas phase nucleation is not controlled, this procedure leads to large concentrations of soot in the deposits. However, when gas phase nucleation is kept to a minimum, "...a singularly nucleated, or substrate-nucleated, pyrolytic carbon (PC)
is formed.\textsuperscript{1}{p. 74} Second, the PC is converted into HOPG by compression annealing. Typically, the PC is subjected to 300-500kg/cm\textsuperscript{2} at 2800-3000°C with a final treatment of 10kg/cm\textsuperscript{2} at 3400°C. Moore reports that this process produces crystals as large as 4\times 2\times 0.1 inches with a mosaic spread of 0.4±0.1°.

A typical specimen in this work was a rectangular solid 2cm on a side and a few millimeters thick. The HOPG was rinsed in isopropanol to remove hydrocarbons. Next, a fresh basal plane was exposed by cleaving the surface with adhesive tape (Scotch brand Magic tape). Then the HOPG was mounted on a Cu disc, fastened down with stainless steel screws and transferred into an ultra high vacuum (UHV) chamber.

These Cu disks were part of transfer system designed by Chottiner et al.\textsuperscript{2, 3} which allowed the sample to be transferred in and out of a UHV chamber without breaking vacuum. In addition, it allowed the samples to be cooled to 100K and heated (by electron beam bombardment from the rear) to 1200K while monitoring sample temperature with a thermocouple junction. The thermocouple pair used in this work was Chromel-Alumel.

After being transferred into the UHV chamber (typical base pressure 2\times 10^{-10} torr), the HOPG was heated until it was a medium orange color. A digital optical pyrometer (Leeds & Northrop model 8646) indicated this to be ~1300K. This temperature agreed within 50° to the thermocouple reading. It was difficult to get a good thermocouple attachment to the HOPG(bp) without noticeably damaging the surface. The best arrangement was obtained by spot welding the thermocouple wires to a backing plate sandwiched between the HOPG
crystal and the Cu disk.

The following elementary analysis leads to the conclusion that the temperature at the backing plate is nearly the same as the temperature of the HOPG(bp) surface. The thermal conductivity of HOPG is highly anisotropic.\(^4,5\) Within the basal plane, the thermal conductivity exceeds 10 watts/cm\(^{-\circ}K\)\(^{12}\) (larger than the conductivity of silver) while in the c-axis direction, the conductivity is <0.2 watts/cm\(^{-\circ}K\). Employing a simple theory which assumes a steady state, the thermal gradient across the sample was calculated. Using a typical electron beam heating power density of 2.5 watts/cm\(^2\), a sample thickness of 0.3cm and a coefficient of thermal conductivity at 150K of 0.12 watts/cm\(^{-\circ}K\), a temperature gradient along the c-axis of 6\(^\circ\) is calculated. Temperature uniformity within the basal plane was checked by color uniformity across the face of the sample. No dark or bright spots were observed.

1.2 ISLAND FORMATION

Pt was loaded onto the HOPG(bp) by thermal vapor deposition. The Pt vapor was established by passing an electrical current through a W filament wrapped with a Pt wire. Two problems were encountered using this technique. First, the Pt formed a eutectic with the W causing the filament to melt as the Pt evaporated. The way this problem was minimized was by finding a combination of W surface area, W volume, and amount of Pt that allowed for several controlled depositions before the filament melted to its center and broke. Several geometries are suggested in the literature\(^6-8\); the
best geometry for this work was obtained using a 2cm length of 0.5mm diameter Pt wire (Johnson and Matthey, 5 9's) wrapped around two parallel pieces of triple braided 10mil W wire (Thermionic Products Inc.). This filament was bent in a "C" shape and inserted into the ends of a 1/4" dual Cu feedthrough.

Second, the Pt tended to "explode" upon melting, shooting molten drops of Pt across the chamber and significantly depleting the Pt available for depositions. It was hypothesized that the cause of the explosion was trapped gas in the Pt wire and this problem was overcome with a two step procedure. Prior to wrapping the Pt, it was pounded flat using a ball peen hammer then cleaned with a soapy solution in an ultrasonic bath. After inserting the oven into the UHV chamber, the filament was degassed at ~1100K (a dull red glow) for 24 hours.

The filament was heated using a sublimation pump power supply (Varian model 922-0006). Filament current was measured using a current shunt (0.5mV/A) and controlled by hand using an external Variac in series with the power supply. Typical currents during evaporation were ~30A and easily controlled to three significant digits. Typical evaporation rates (as determined by XPS) were ~10^{12} atoms/sec. Indiscriminate deposition of Pt was prevented by placing a Cu cylinder around the Cu feedthroughs to which the filament was attached. The flux to the substrate was collimated by a 1/2" diameter stainless steel tube attached to the front of the cylinder.

Pt loading was measured using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). XPS proved to be
a much superior technique because the ratio of the relative sensitivities of Pt/C is 100 times larger for XPS compared with AES. Using these techniques, no impurities were found on the Pt/HOPG(bp) surfaces. C impurities were checked for by depositing Pt on a Ag substrate. Again, nothing but Pt was found on the surface.

2 SAMPLE ANALYSIS

2.1 X-RAY PHOTOELECTRON SPECTROSCOPY

XPS analysis was performed in a custom Perkin Elmer multitechnique chamber (chamber A). The photon source was a dual anode X-ray gun (Phi model 04-548). A Mg anode was used for this work. The gun was operated with the anode at 15kV and at a power of 400 watts. The incident angle of the photons was typically 55° and the takeoff angle of the photoelectrons 0° (both angles measured with respect to the sample normal). Photoelectrons were energy analyzed using a 27.9cm radius hemispherical analyzer (Phi model 10-360) operated in the fixed analyzer transmission mode. Early data (up to 2/12/89) was taken using a lens with a fixed spot size (0.9cm x 0.3cm). Later, a variable spot size (0.02cm radius to 0.3cm x 0.1cm) lens was installed. The analyzer was calibrated with respect to energy resolution using a Ag sample, Table 2.1.

Data analysis (curve fitting, peak position, peak area, background subtraction) was accomplished using Phi's standard 5000 series software package running on an Apollo workstation.
## Table 2.1

<table>
<thead>
<tr>
<th>Spot Size (mm)</th>
<th>Pass Energy (eV)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0 X 3.0</td>
<td>8.95</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>17.90</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>35.75</td>
<td>1.00 (*)</td>
</tr>
<tr>
<td></td>
<td>89.45</td>
<td>1.76 ($)</td>
</tr>
<tr>
<td>1.1</td>
<td>8.95</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>17.90</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>35.75</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>89.45</td>
<td>1.70</td>
</tr>
<tr>
<td>0.6</td>
<td>17.90</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>89.45</td>
<td>1.7</td>
</tr>
<tr>
<td>0.2</td>
<td>17.90</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>35.75</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>89.45</td>
<td>1.64</td>
</tr>
</tbody>
</table>

* setting used for high resolution small energy range scans.
§ setting used for survey scans

XPS instrument resolution as a function of spot size and pass energy.
Pt XPS signal intensities were converted into coverages using the following photoelectron intensity equation

\[ dN_i = \Phi(x,y,z)\rho_i d\sigma_i P_i \Omega(\text{IRF}) \]  \hspace{1cm} \text{eq. 1}

Where:

- \( N_i \) = Number of counts of the \( i^{th} \) atomic species
- \( \Phi \) = X-ray flux at the position \((x,y,z)\)
- \( \rho_i \) = Number of \( i^{th} \) species in the volume \((dx,dy,dz)\)
- \( d\sigma_i \) = Differential cross section for photoionization of \( i^{th} \) species
- \( P_i \) = Probability an electron will escape from \((x,y,z)\) without loss of energy \((P_i = \exp(-z/\lambda \cos \theta))\)
- \( z \) = distance from \((x,y,z)\) to surface of sample
- \( \lambda \) = mean free path of photoelectron of interest
- \( \theta \) = angle between photoelectron velocity and sample normal
- \( \Omega \) = Acceptance solid angle of analyzer
- \( \text{IRF} \) = Instrument response function.

Table 2.2 lists the values assigned to each of these parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d\sigma_{pt} )</td>
<td>0.352</td>
<td>15</td>
</tr>
<tr>
<td>( d\sigma_c )</td>
<td>0.0219</td>
<td>15</td>
</tr>
<tr>
<td>( \lambda_{pt} )</td>
<td>2.2nm</td>
<td>16</td>
</tr>
<tr>
<td>( \lambda_c )</td>
<td>1.8nm</td>
<td>16</td>
</tr>
<tr>
<td>( \rho_{pt} )</td>
<td>0.09Å⁻³</td>
<td>17</td>
</tr>
<tr>
<td>( \rho_c )</td>
<td>0.15Å⁻³</td>
<td>17,18</td>
</tr>
</tbody>
</table>

Parameter table for XPS coverage estimates of Pt on HOPG(bp).
Equation 1 was then integrated assigning the HOPG(bp) surface to 
z=0 and assuming a continuous uniform Pt overlayer of thickness t 
giving

\[ N_{pt} = 0.69[1-\exp(-t/22)] \quad \text{eq. 2} \]
\[ N_c = 0.058\exp(-t/22) \quad \text{eq. 3} \]

\( \phi \) and IRF have been omitted because they cancel out in the next 
step. Dividing \( N_{pt} \) by \( N_c \) and solving for \( t \) gives

\[ t = -22\ln[0.084(N_{pt}/N_c) + 1]^{-1} \quad \text{eq. 4} \]

This \( t \) was then divided by the atomic diameter of Pt (2.78Å) to 
give the monolayer equivalent coverage. Thus, a Pt loading 
reported in this work as 50% would yield a \( t=1.39\text{Å} \).

The atomic diameter of Pt was used because it was originally 
thought that at the lowest coverages single Pt atoms would be 
populating the HOPG(bp) surface. It is reasonable to ask how much 
the calculated coverages would differ if Pt-Pt distances typical of 
surfaces terminating bulk structures were used. The spacing of 
atoms on such a surface will usually be smaller than the atomic 
radius of the atom. The closest Pt-Pt spacing, reported by Van 
Hove et al. for the Pt(100) surface, is 1.96Å.\(^{19} \) Using this value 
along with a spherical atom approximation to calculate \( s_{pt} \) leads to 
a reduction in the calculated ZML of -50%.
For elements other than Pt, signal intensity is reported as a percentage of the total XPS signal. These percentages were calculated using a four step procedure. First, the area of each major peak in the spectrum was measured after a linear background had been subtracted. These areas were divided by the time of collection and multiplied by the pass energy to account for a 1/E instrument response function. Second, each area was divided by the sensitivity factor of its corresponding element (C = 0.296, O = 0.711). Third, the normalized areas were added to give the total XPS signal. Fourth, the peak area of any given element was calculated as a percentage of the total XPS signal.

2.2 AUGER ELECTRON SPECTROSCOPY

AES analysis was performed in another custom made Perkin Elmer chamber, chamber B. Auger transitions were produced by an electron beam from an electron gun (VSW model EG5). Typical beam conditions were: 1.5mm spot size, 3kV, 3µA sample current. Sample current was crudely measured by biasing the sample to 50V with respect to earth ground and then measuring the current flowing between the sample and ground. AES electrons were energy analyzed using a 10cm radius hemispherical analyzer (VSW model HA100). Output from the analyzer's electron multiplier was measured using phase sensitive detection with the sample modulated by a signal of 5V peak-to-peak at 5kHz. The lock-in amplifier (EG&G model 5705) output was recorded on an XY recorder producing the standard dN/dE vs. E AES plot. The sensitivity of this system was relatively poor for Pt making it difficult to routinely detect <20% of a monolayer of Pt.
The AES coverages in this work were calculated with the following four step procedure. First, the peak-to-peak heights of each element's major peak in the spectrum were measured. Second, each peak was divided by the sensitivity factor of its corresponding element (C = 0.18, O = 0.50, Pt = 0.035). Third, the normalized peak-to-peak heights were summed to give the total AES signal. Fourth, it was assumed that the surface atoms were responsible for 1/3 the total AES signal; so a given element's normalized peak-to-peak signal was divided by 1/3 the total signal to give the percent of a monolayer for that element.

2.3 THERMAL DESORPTION SPECTROSCOPY

Temperature programmed desorption (TPD) experiments were also carried out in chamber B. A typical TPD experiment started by filling a calibrated volume (27.4 cm³) to a pressure measured with a capacitance manometer (MKS model 270B controller, 390HA-000001 head). The number of molecules in the volume was then calculated using the ideal gas law. The volume was connected to the main chamber via a glass capillary array 1.3 cm in diameter and 0.2 cm thick (Galileo Electro-Optics model C13S20M50). The array consists of hexagonally arranged 50 μm diameter tubes spaced ~100 μm apart. The sample was placed ~1 cm from the array and dosed by opening an all metal valve (Nupro model SS-4H-TH3) located between the array and the calibrated volume. For a dose equivalent to 10L of backfilling, this procedure decreased the total number of O₂ molecules needed by a factor of >50.
Next, the sample was rotated in front of a mass spectrometer head (Dycor model M200M with the MO00T Time Display Option). The mass spectrometer head was covered by a stainless steel collimator with an ~1cm diameter tube attached to the end of the cylinder. This reduced the signal due to gas desorbing from the sample holder, heater filament, and other surfaces not in direct line of site of the collimator tube. The sample was then heated by increasing the current through the electron beam heater filament. Control of the heating rate was by hand using an XY recorder to monitor the thermocouple voltage as a function of time. The mass spectrometer was able to follow the partial pressures of up to five masses as a function of time. Simultaneously, a personal computer (IBM XT) connected to the thermocouple junction via an A/D converter (Keithley model 570) and a digital voltmeter (Keithley model 177) used as an amplifier, collected the sample temperature as a function of time. After a heating run, the mass spectrometer’s buffer was dumped to the computer and merged with the temperature data to form pressure vs. temperature plots. The computer/mass spectrometer interfacing, data analysis and plotting were all done with software written using the ASYST software package.

The peak position of a TPD curve was found by smoothing the data until just before the smoothed curve’s intensity began to drop below that of the raw data. This smoothed curve was then used to find peak positions. No curve fitting was attempted. To find the area beneath a peak, first the curve was smoothed; then a linear background was subtracted; finally, this peak was numerically
integrated using the 1/3 Simpson's Rule.

2.4 SCANNING TUNNELING MICROSCOPY

2.4.1 THEORY

Because of Scanning Tunneling Microscopy's relatively recent appearance in the surface science arsenal of techniques, it seems appropriate to include a brief description of the theory of operation. The fundamental basis of STM is that when a sharp tip is brought in proximity to a surface, electrons can travel between the two pieces of matter by the tunneling process. The extremely high resolution of the technique in the direction along the surface normal is due to the exponential relation between sample current and tip-sample separation. High resolution within the plane of the surface is thought to be the result of tunneling to or from a highly localized ($p_z$ or $d_z$) state of the tip apex.\(^{67}\)

When the STM was first introduced as a surface science tool in 1982,\(^7\) the simple theory of one dimensional tunneling through a planar barrier was used to model the tunneling current (J),

$$J \propto \exp(-A \phi^{1/2} s)$$  \hspace{1cm} \text{eq. 5}

With: \(A = \frac{1}{h\sqrt{8m}} = 1.025\text{Å}^{-1}\text{eV}^{-1}\)

\(\phi = \text{Tunneling barrier (work function in this case)}\)

\(s = \text{Distance between planes.}\)

This model is useful for determining orders of magnitude in the tunneling current and in what direction the tip will move as
tunneling current and bias voltage are varied. For example, using the work function of carbon (5eV), the change in current upon a 0.2nm rise (an atomic step) is two to three orders of magnitude (depending on whether a 0.1nm or 1.0nm average tip/surface separation is assumed). The planar model, however, does not address the fact that tunneling occurs between electrons at the Fermi level and that these electrons may have their own complicated spatial distribution. Thus, in order to model the topographs obtained using STM, a more complete theory is needed. Perturbation theory has been most successful in explaining some STM results. It is found that 1st order perturbation theory is almost exact in its calculation of tunneling current, yielding

\[
J = \frac{4\pi e}{h} \sum_{\mu,\nu} f(E_{\mu})[(1-f(E_{\nu} + eV))]|M_{\mu\nu}|^2 \delta(E_{\mu} - E_{\nu})
\]

where: \( f(E) \) = The Fermi function
\( V \) = Applied voltage
\( M_{\mu\nu} \) = Tunneling matrix element between the state \( \psi_{\mu} \) of the probe tip and the state \( \psi_{\nu} \) of the sample
\( E_{\nu} \) = Energy of the state \( \psi_{\nu} \) in the absence of tunneling.

Tersoff and Hamann point out that while this resembles ordinary 1st order perturbation theory, it is different in that \( \psi_{\nu} \) and \( \psi_{\nu} \) are nonorthogonal eigenstates of different Hamiltonians. Bardeen, using the WKB method, showed that the tunneling matrix elements can be computed using
\[ M_{\mu \nu} = \int_{S} \left[ \Psi^*_{\mu} \nabla \Psi_{\nu} - \Psi_{\nu} \nabla \Psi^*_{\mu} \right] \]

where \( \Psi_{\nu} = \) The wave function
\( S = \) Any surface entirely within the tunneling gap.

Bardeen points out that the term in square brackets is just the current operator. Tersoff and Hamann have started with this theory and made the following assumptions:\(^{52}\)

1. Limit of low temperature (valid assumption since most experiments are done at room temperature where \( kT \ll \) work function)

2. Limit of small voltage (also a good assumption as common bias voltages are in the .01V to .1V range)

3. The tip is modelled as an s-wave

4. The surface is expressed as a Bloch wave expansion.
They then obtain the following expression for the tunneling current:

$$I = 32n^3(2\pi/h)e^2V\phi^2D_t(E_F)R^2\kappa^{-4}\exp(2\kappa R) \sum \psi_v(r_0)^2 \delta(E_v - E_F)$$  \hspace{1cm} \text{eq. 8}$$

Where:

- $D_t$ = Density of states per unit volume of probe tip
- $R$ = Local radius of curvature of the tip
- $r_0$ = position of center of tip
- $\kappa$ = minimum inverse decay length for the wave functions in vacuum = $2\pi/h(2m\phi)^{1/2}$.
- $\phi, V, \psi, E_v$ as in eq's. 5-7

Next, they insert typical metallic values for $D_t$ and $\phi$ to arrive at the tunneling conductance

$$\sigma = 0.1R^2\exp(2\kappa R)\rho(r_0, E_F)$$  \hspace{1cm} \text{eq. 9}$$

$\rho(r_0, E_F) = \text{surface local density of states}$

$$= \sum \psi_v(r_0)^2 \delta(E_v - E_F)$$  \hspace{1cm} \text{eq. 10}$$

with distances in au, energy in eV and conductance in ohm$^{-1}$. 

Tersoff further calculated the difference between having a tip $\Psi$ resulting from completely coherent states in the tip ($k_{td} < < 1$) and a $\Psi$ resulting from completely incoherent states ($k_{td} > > 1$) ($k_t = \text{Fermi wave vector}$, $d = \text{length scale describing area over which}$
appreciable tunneling current flows on tip \( - (R/k)^{1/2} \). In normal metals, \( k \alpha d < 1 \) therefore neither extreme holds. Tersoff expected the STM current to vary linearly with \( k \alpha d \). He found that for metals the difference is quite small. However, for semi-metals and semi-conductors the difference is large and must be taken into account.

The above theory has been applied to HOPG(bp) by Tomanek et al. to account for the asymmetry in tunneling current intensity between \( \alpha \) sites (those with an atom beneath them) and \( \beta \) sites (those without an atom beneath them). They define the unit cell as in Figure 2.1 and point out that the Fermi surface of graphite lies near the line in reciprocal space: \( k = (1/3, 1/3, \zeta) \). Next, they write the eigenstates of the HOPG as a linear combination of Bloch functions localized on the sites \( \alpha, \alpha', \beta, \beta' \). Finally, they show that the Hamilton matrix, \( H_{ij}(k) = \langle \Phi_i | H | \Phi_j \rangle \) is given, in the nearest neighbor approximation, by

\[
H(1/3, 1/3, \zeta) = \begin{pmatrix}
\alpha & \alpha' & \beta & \beta' \\
\alpha & E_\alpha & t_\alpha(\zeta) & 0 & 0 \\
\alpha' & t_\alpha^*(\zeta) & E_\alpha & 0 & 0 \\
\beta & 0 & 0 & E_\beta & 0 \\
\beta' & 0 & 0 & 0 & E_\beta \\
\end{pmatrix}
\]

The total decoupling of the \( \alpha \) states from the \( \beta \) states is the result of cancellation of phase factors during the Bloch wave expansion. This cancellation is true throughout the crystal to all
Figure 2.1 "Schematic diagram of two successive layers of hexagonal graphite in (a) top view, and (b) side view. The unit cell is enclosed by a dotted line in (b)."
(Text and figure from ref. 19.)
orders of neighbor interactions. A further result of this phase
cancellation is that $\beta$ atoms in one plane do not interact with $\beta$
sites in neighboring planes leading to a diagonal $\beta$ submatrix. The
authors finally conclude that "... this Hamiltonian gives rise to a
doubly degenerate band at $E=E_\beta$ near $E_F$ with wavefunctions localized
on the $\beta$ sites, and to a dispersive band with wavefunctions
localized on the $\alpha$ sites." In the small applied voltage limit, the
STM only samples a narrow region of energies below $E_F$. It is
sensitive to all the $\beta$ states but only a small number of $\alpha$ states.
It is stressed that this is an effect of the density of states and
not due to the spatial extent of the wavefunctions. In addition,
it is a bulk effect that is seen also at the surface and not just a
surface effect.

The above arguments are quite beautiful and it is gratifying
to see such a simple solid state theory model experimental results
so well. Unfortunately, the theory of STM has not proceeded to a
point where predictions can be made about islands containing many
dozens of atoms sitting on a surface. Thus, the work done in this
thesis is of an observational nature and no attempt is made to
calculate theoretical topographs of the surface.

2.4.2 PRACTICAL CONSIDERATIONS

Scanning Tunneling Microscopy results reported here were taken
using a bench top microscope (Digital Instruments, Nanoscope II).
The Pt/HOPG(bp) surfaces were also examined with several other
instruments (Jayne Inc. Prototype, Digital Instruments Nanoscope I,
and a microscope built by Michael Green at Stanford). The results
from these other instruments were consistent with those of the Nanoscope II.

The Nanoscope II uses a piezoelectric cylinder to scan the tip across the sample. The tubes come in different lengths allowing for different combinations of sensitivity and maximum scan size. In this work, a 0.5µ maximum scan size tube was used to obtain images when sub-atomic resolution was required. An 8µ maximum scan size tube was used to obtain images over larger areas. The tips were mounted on the tube by a small Macor™ piece fixed to the perimeter of the tube. Embedded in the Macor was a small metal tube into which a piece of 10mil wire was inserted after the wire was prepared to have a sharp tip.

A "good tip" was characterized by two properties. First, when the tip began tunneling it gave a relatively noise free tunneling current signal. This was ascertained by bringing the tip within tunneling distance of the surface and then maintaining a stationary position with respect to the surface plane. The distance between tip and surface was then monitored with respect to time. If the time averaged signal corresponded to <0.2Å peak-to-peak deviation from the average distance, the tip was considered noise free. Second, when the tip was scanned across a graphite surface it yielded as an image a hexagonal array of bright spots with the distance between spots of ~0.28nm. A tip satisfying both of these conditions was capable of imaging small metal clusters (1 to 500Å in diameter) on HOPG(bp). It was difficult to obtain a tip that satisfied both of these conditions. For scans where sub-atomic resolution was not required, the graphite resolution condition was
sometimes relaxed.

Two types of wire were used to make tips, W and a Pt/Ir (80/20) alloy. The W tips were prepared by etching in a 4M KOH solution. The wire was cut to a length ~0.5cm longer than necessary for the final tip. This wire piece was then inserted into a dip socket used as an easy means of delivering a current to the wire and to physically hold the wire in place protruding ~0.5cm into the solution. A 30V AC current was then passed between the wire and a cylindrical Pt grid ~5cm in diameter immersed in the solution around the wire. Etching was continued until the wire tip was completely out of the solution as evidenced by a cessation of noise, bubbles and fumes emanating from the wire/solution interface (~60s). The wire was then dipped ~1mm into the solution and a current passed for ~1sec. The wire was next rinsed in distilled water and dried in an N₂ gas flow. Most of the early STM work was done using this type of tip. However, it was found that these tips were better for imaging objects 100’s to 1000’s of angstroms in size. To image smaller objects, the Pt/Ir tips were more reliable.

The Pt/Ir tips were initially purchased from Digital Instruments. About 20% of the time, these tips gave atomic resolution images as received. The tips that did not work and old tips that had sustained a "crash" could be rejuvenated. This was accomplished by holding the wire with a pair of pliers, grasping the end of the wire with a pair of wire cutters at a 45° angle, and then pulling the wire until it broke. It was important not to cut the wire but instead to draw it to get a good tip. If this drawing process was done just prior to using the tip, it was necessary to
bring the tip into tunneling range of the surface and then quickly withdraw it four or five times. Omitting this step almost always resulted in a tip crash upon first engagement of the tip to tunneling. This procedure also had a success rate of ~20%. These tips looked much more blunt and rough than the etched W tips but when they worked, they usually gave sub-atomic resolution.

2.5 CYCLIC VOLTAMMETRY

Electrochemical measurements were done using the cyclic voltammetry (CV) technique. For the in-situ work, a Pine RDE 4 potentiostat was used. The Ex-situ work was done using a ParC model 173 signal generator along with a ParC model 175 potentiostat. The in-situ cell was constructed by surrounding a 0.5mm diameter Pt wire with a piece of PFE/PTFE single lumen heat-shrink tubing (Zeuss Inc.). After this tube was shrunk about the Pt, a 0.5mm diameter Pd wire was held against the outer surface of the shrunk tubing parallel to the Pt wire. A second piece of shrinkable tubing was placed around the entire assembly and a cut was made normal to the long axis of both wires thus exposing the ends of the two wires separated by the PFE/PTFE material. This piece was then press fit into a larger Teflon block and set with the ends of the two wires just below the block’s surface. The Teflon block was mounted on the end of a magnetically coupled manipulator which allowed it to be transferred from its electrolyte loading position to a location just beneath the sample surface in the auxiliary chamber. Electrical connections to the cell were made using Teflon coated wire that was coiled around the transfer
rod allowing it to expand and contract as the cell was moved in and out of the auxiliary chamber. The description of a typical experiment using this system follows.

Electrolyte was delivered to the cell using an all Teflon delivery system. The electrolyte was stored in Teflon cylinders kept inside a plexiglass box that was filled with N₂ gas. The electrolyte flow was controlled using a gas tight syringe to raise and lower the pressure in a system of tubes and valves so that a small quantity of liquid could be removed from the cylinder and transferred to a tube suspended in a UHV 6-way cross just above the cell. In this way, one or two drops of electrolyte were delivered to the cell which was maintained in an N₂ atmosphere.

The Pd wire was then charged with H₂ by using the Pine potentiostat in the galvanoostatic mode. Charging was accomplished using ten cycles of -50μA for 20sec then +20μA for 30 sec then a final cycle of -100μA for 3 minutes and +20μA for 5 sec. As long as the working electrode was not cycled into the O₂ evolution region, this charging produced a stable reference electrode.

After the Pd was charged, the electrolyte was removed using a Teflon tube connected to a hand pump (Nalgene Inc.). The tube was attached to the system via a bellows that allowed it to be lowered to remove the electrolyte and raised out of the way when not needed. The cell was then rinsed a few times by delivering and removing a few drops of electrolyte.

Next, a drop of electrolyte was delivered and a Ni wire, attached to the same bellows as the withdrawing tube, was lowered into the electrolyte. The cyclic voltammogram of this wire was
used to check for proper operation of the cell before using the Pt/HOPG(bp) surface. After determining that the cell was usable, the electrolyte was removed and a fresh drop delivered.

The Pt/HOPG(bp) surface which had been previously prepared, was now transferred from the main chamber onto a sample stage capable of being rotated through 90° in the auxiliary chamber. The sample was then rotated so that its surface normal was pointing down. The auxiliary chamber was then backfilled with N₂. Using a standard viscous flow regime argument, it was determined that a molecule desorbing from the auxiliary chamber wall would take approximately 270 sec. to travel to the center of the chamber. A flow rate of 50ft³/hr was sufficient to exchange the entire volume of the auxiliary chamber in this time. Using a two stage regulator on the N₂ cylinder and a carbon vane pump at the outlet of the auxiliary chamber, this flow rate was maintained while the chamber pressure was held near atmospheric pressure. Thus, contamination of the electrolyte was held at a minimum. The electrolyte drop maintained its volume under these conditions for ~30min. After this time, a visible change in the amount of electrolyte was observable.

Finally, the gate valve between the cell preparation chamber and the auxiliary chamber was opened and the cell transferred so that the drop was centered on the HOPG crystal. The rotatable sample stage was attached to a bellows sealed linear/rotary manipulator allowing it to be lowered until it made contact with the electrolyte. It was important to have a cell design that produced a small electrolyte drop so that the edge sites of the
HOPG were left dry. With bare HOPG, this was not a problem because the surface is hydrophobic, thus preventing the spread of the electrolyte to the edges. With Pt adsorbed, however, the surface becomes hydrophylic drawing the electrolyte to the edges as far as surface tension will allow.
CHAPTER III
RESULTS AND DISCUSSION

1 XPS AND AES OF HOPG(bp)

1.1 SURVEY SCANS

The UHV portion of each experiment began with an XPS or AES survey scan of an HOPG(bp) surface just after it was transferred into the chamber, Figures 1.1 and 1.2. Below is an analysis of the surface impurities indicated by these two techniques. A discussion of how much the HOPG(bp) deviates from a perfectly crystalline surface is also provided. In addition, some of the vagaries of the Auger spectra are pointed out.

The initial XPS scan usually contained a peak in the oxygen region. When present, the oxygen accounted for 0.8%(±0.2%) of the total XPS signal. This percentage is the mean of five independent measurements and the ± value is the square root of the their variance. The oxygen peak intensity always decreased upon flashing the HOPG to ~1000K. The magnitude of this decrease was such that, under the same XPS data collection conditions used before heating, no oxygen peak above the background was measurable. If one half the peak-to-peak noise signal is taken as the point at which an oxygen peak is considered clearly identifiable, then heating the surface reduces the oxygen signal below 0.06%(±.04%). In their critical review of XPS and AES, Powell and Seah indicate that this
Figure 1.1  XPS survey scan of bare HOPG(bp).
Figure 1.2  AES survey scan of bare HOPG(bp).
is indeed an upper limit of the oxygen signal and that a more sophisticated analysis would lead to an even smaller oxygen percentage.\textsuperscript{20}

As shown in Figure 1.1, oxygen is the only impurity found on the HOPG(bp) surface. No trace metals or other elements were found. It is also clear from this spectrum that the region in which the Pt 4f peaks occur (60eV-80eV) is featureless and has low intensity.

1.2 CARBON 1S PEAK

The C 1S XPS peak was used as a reference with which all other peak positions were compared. The procedure used was to first set the C 1S peak = 284.3(\pm 0.2)eV\textsuperscript{21} and then to measure the positions of other peaks with respect to this reference. Any drift in the position of the C 1S peak from sample to sample was assumed to be the result of the spectrometer electronics or perhaps a change in the work function of the analyzer. The C 1S peak did not shift, within the resolution of the analyzer, from day to day. It did shift from month to month because routine recalibration of the instrument was not performed.

The C 1S peak does show some structure. There is a high binding energy shoulder which results from a \Pi' shake-up peak commonly found in carbon spectra.\textsuperscript{22} Diebold et. al have used angle resolved HREELS to identify several plasmon losses that could also contribute to this shoulder, Table 1.1\textsuperscript{23}
| Transition (q||c-axis) | Transition (q||c-axis) | Transition Energy (eV) |
|----------------------|----------------------|------------------------|
| Interband Transition $\Pi\rightarrow\Pi$ | | 4.7 |
| Surface Plasmon | | 6 |
| $\Pi$ Bulk Plasmon | | 7.05 |
| Interband Transition $\sigma\rightarrow\sigma$ | | 14.4 |
| Surface Plasmon | | 17.7 |
| $\Pi$ and $\sigma$ Bulk Plasmon | | 26 |
| Interband Transition $\sigma\rightarrow\Pi$, $\Pi\rightarrow\sigma$ | | 4 |
| Intertransition | | 11 |
| Surface Plasmon | | 12 |
| Bulk Plasmon | | 15.5 |
| Bulk Plasmon | | 18 |

Diebold et al.'s plasmon losses from the graphite surface as determined by HREELS.\textsuperscript{23}

It was not possible to curve fit over the entire energy range of these plasmon losses due to restrictions imposed by the Perkin Elmer software package. Instead, all C peaks were fit with two curves separated by 6.7eV as suggested by the PHI Handbook of X-ray Photoelectron Spectroscopy.\textsuperscript{22} The full width at half maximum of the fitted 1S peak averaged over 34 spectra taken from 10 different surfaces was 1.12eV (±0.11eV). It should be noted that the data
was digitized upon collection into bins that were 0.05eV wide.

1.3 HOPG(bp) VALENCE BAND

The valence band region of the XPS spectrum for HOPG(bp) was also recorded, Figure 1.3(A). It clearly shows that the density of populated states slowly approaches zero near zero binding energy. This is consistent with HOPG's semimetal electronic behavior. The low intensity and relatively featureless contribution that HOPG(bp) makes to the XPS valence region makes this substrate ideal for examining the evolution of metal island band structure on the surface. This is in sharp contrast to the alumina surface on which other workers have measured the effects of small Pt islands on the valence region spectra, Figure 1.3(B).²

1.4 AES

AES analysis of the HOPG(bp) was more complicated than the XPS analysis. Figure 1.2 is representative of a spectrum collected just after the sample was transferred into the UHV chamber. Again, Carbon and oxygen are the only elements present in the spectrum. The sharp pre-peak features near the main C(272eV) peak are indicative of graphitic carbon.²⁴⁻²⁶

1.5 OXYGEN

As shown in Figure 1.4, heating the surface to ~1000K reduces the oxygen peak significantly. The oxygen in Figure 1.2 (an unheated surface) accounts for 1.3% of the total AES signal. Using the same 1/2 peak-to-peak noise condition as with the XPS data
above (Chapter II, section 1.1), it can be concluded that any oxygen in Figure 1.4 (a heated surface) accounts for <0.4% of the total AES signal.

The questions arise from these XPS and AES spectra as to what kind of oxygen is populating the HOPG(bp) surface and where it is adsorbed. It is likely that the oxygen exists at defect sites because the pristine basal plane's lowest energy electronic states available for bonding (the \( \pi^* \) orbitals) are so high in energy. The electron spectroscopies then give a lower bound on the number of defect sites present on a freshly cleaved surface of \(-1\%\).

It is natural to speculate on the type of defects that may exist on the HOPG(bp) surface. As described in the experimental section, HOPG is a mosaic material. Low Energy Electron Diffraction (LEED) of the surfaces used in this work usually showed a ring populated by \(-96\) bright dots. The background intensity was usually low. Since the incident electron beam used in these LEED experiments is known to be \(1\)mm in diameter, there are a minimum of \(16\) differently oriented crystalline domains/mm\(^2\) on the surface (this assumes that a single graphitic domain would yield \(6\) spots in the LEED pattern). This corresponds to a domain size no larger than \(0.25\)mm. If the simple model that the domains are square in shape is used and it is assumed that there are no inter-domain sites, then the ratio of defects to total sites should be \(4\pi a/l^2\) with: \(l=\)domain length, \(a=\)the C-C bond length and the assumption that the carbon atoms are spheres with radius = \(a\). Taking \(l=0.25\)mm and \(a=0.142\)nm, it is calculated that at least \(7\times10^{-4}\%\) of the surface sites are defect sites. Unless there are \(-1000\) domains
Figure 1.3 XPS spectra of the valence band regions of HOPG(bp), A, and alumina, B.

N(E) in arbitrary units

Binding Energy (eV)
Figure 1.4 AES survey scan of HOPG(bp) after heating the surface showing the lack of an O signal.
of each orientation or each defect has an effective radius of ~20 atoms, this model alone does not account for the 1% value obtained from electron spectroscopies.

Another possible location for defect sites is within the domains themselves. The triangular net of C atoms on the surface may be broken in some places. The C atoms at these locations would then have dangling bonds that could react with atmospheric gases to form functional groups such as quinone or hydroquinone.

In an attempt to ascertain what chemical state the oxygen on the surface was in, three of the oxygen spectra were curve fit. Figure 1.5 is a typical oxygen spectrum. The full width at half maximum of this peak is ~3.3eV suggesting that there are two or perhaps three oxygen species present on the surface. It was not possible to obtain a good fit for all three spectra using only two peaks. Thus, the spectra were fit with three peaks each. The means of the fitted peak positions were:

**TABLE 1.2**

<table>
<thead>
<tr>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>533.7±.2eV</td>
<td>532.2±.06eV</td>
<td>530.8±.06eV</td>
</tr>
</tbody>
</table>

0 1S peaks seen on bare HOPG(bp)

The highest binding energy peak matches reasonably well with both \(^{27}H_2O(533.2eV)\) and hydroquinone(533.5eV).\(^{27}\) The 532.2eV peak matches well with Ohta et al.'s p-benzoquinone.\(^{28}\) The 530.8eV peak
Figure 1.5  XPS scan of the O region on a bare HOPG(bp) surface. The solid lines represent the best-fit curve and its constituents.
does not match well with any reasonable choice of molecule in the PHI library. Table 1.3 contains the O 1S binding energies for a few oxygen containing molecules not listed in the PHI library. Since C 0 and possibly H are the only atoms present according to the XPS survey scans, only molecules with these constituents need be considered. To illustrate the size and direction of the shift induced when these molecules are adsorbed on a surface, the CO/Ni and CO$_2$/Ni O1S binding energies are included. Note that the shifts are toward lower binding energy. Thus, molecules with gas phase binding energies $<$530.8eV probably need not be considered.

**TABLE 1.3**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Gas Phase Binding Energy (eV)</th>
<th>Ni Adsorbed Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>543.1</td>
<td>-----</td>
</tr>
<tr>
<td>CO*</td>
<td>542.3</td>
<td>531.4</td>
</tr>
<tr>
<td>CO$_2$*</td>
<td>541.3</td>
<td>534.4</td>
</tr>
<tr>
<td>CH$_3$OH$^*$</td>
<td>538.9</td>
<td>-----</td>
</tr>
<tr>
<td>CH$_3$CHO$^*$</td>
<td>537.6</td>
<td>-----</td>
</tr>
</tbody>
</table>

*=$reference 29,  $=$reference 30

O 1S binding energies for a few molecules not listed in the PHI library.
It is evident from Table 1.3 that there are several candidates for the functional groups on the HOPG(bp) that could have O1s binding energies consistent with those observed in this work. The C1s signal from these functional groups would give further information about chemical structure. However, the large C1s signal from the HOPG makes it very difficult to measure small C signals from the defect sites. Vibrational spectroscopies such as HREELS and IR would help considerably in identifying the oxygen containing molecules on the surface.

The effect of leaving a freshly cleaved HOPG(bp) in air for extended periods was examined using one sample. This sample was cleaved in air and then transferred into the UHV chamber. The initial XPS spectrum showed ~1% oxygen. The sample was then flashed to ~1000K. The subsequent XPS spectrum showed no oxygen. The sample was then transferred out of the chamber and left in a plexiglass box for 122 hours. Transferring the sample back into UHV and taking an XPS spectrum revealed ~1% oxygen. The peak was fit well with the three peak positions listed above in Table 1.2. The sample was then heated to ~1000K. Surprisingly, the XPS spectrum still showed ~1% oxygen. The oxygen peak was fit well with the same three peaks. However, there was a marked increase in the intensity of the 530.8eV peak with respect to the other two peaks. This result may be related to the following observations. After several days in air, it becomes very difficult to obtain atomic resolution on an HOPG(bp) surface using a scanning tunneling microscope. In addition, Bae reports that after several days in air, the Infra Red spectrum of HOPG(bp) shows a distinct carbonyl
band. He also sees an increase in the double layer current of HOPG’s cyclic voltammogram.\textsuperscript{31} It is not clear at this time what the difference is between the oxygen present on an HOPG(bp) surface exposed to air for \(-10\) min. as opposed to \(10^3\) min. The effects of air exposure on samples containing Pt will be discussed later.

1.6 AES ANOMALIES

About half of all the HOPG crystals examined contained AES peaks around 45 eV and 63 eV. Figure 1.6 is an example of such a spectrum. These peaks were unchanged by: cooling the sample to 100K, heating the sample to 1000K, and changing the incident beam energy from 3 kV to 4 kV. That these peaks persist after heating and that no other higher energy AES peaks are found suggest that they are not due to surface impurities. The lack of change upon raising the incident beam energy by 25\% rules out any effect directly related to the incident beam. It is consistent with these results to conclude that the peaks are due to diffraction of secondary electrons by the HOPG crystal. Peaks similar to those in the HOPG spectrum were seen with Ni and positively identified as diffraction peaks by heating. Angle resolved AES experiments or heating close to the Debye temperature of HOPG (~2000K) would be two ways to confirm that these are diffraction peaks.
2 Pt/HOPG(bp)

After the HOPG(bp) had been heated to ~1000K then cooled back to room temperature, Pt was vapor deposited on the surface. In order to control the amount of Pt loaded onto the surface, the evaporations were done in a stepwise manner. Between each exposure to the oven, an XPS spectrum of the surface was recorded. This generated a set of data representing successively higher loadings of Pt on the same substrate. The means of the Pt peak positions and widths of this entire data set (34 spectra) are listed in Table 2.1 along with the spread in the data (± values) obtained using their variances. If Pt/HOPG(bp) is a system like those reported in the literature (ex. Pt/amorphous C, Pt/Graphite Foil, Pt/Teflon), then different Pt coverages should correspond to different size islands. This distribution of islands should in turn lead to a spread in the XPS peak positions and widths. The Pt coverages used in this work (<1%ML to >100%ML) correspond to other work\textsuperscript{5,32} that gave shifts in peak positions of as much as 1eV.

**TABLE 2.1**

<table>
<thead>
<tr>
<th>Peak Center (eV)</th>
<th>FWHM (eV)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4f5/2</td>
<td>4f5/2</td>
<td>4f7/2</td>
</tr>
<tr>
<td>70.77 ±0.20</td>
<td>1.62 ±0.26</td>
<td>1.68 ±0.24</td>
</tr>
</tbody>
</table>

Means of the Pt 4f peak positions and FWHM.
2.1 Pt 4f PEAK SHIFTS

It is evident from the ± values in Table 2.1 that there is not much variation in the spectra upon loading the Pt onto HOPG(bp). However, if the CLS FWHM variance (0.1eV) is used as a measure of experimental error, then the spread in data is about twice that expected due to experimental noise. This could easily be explained by the fact that the signal to noise ratio of the Pt peak is about 8X smaller than that of the C peak. Thus, uncertainties in the Pt peak parameters are greater than those in the C peak. To evaluate the effect of noise on determining peak positions and widths, a numerical value was assigned to the uncertainty in the peak fitting procedure using the following procedure:33,34

1) The best fit curve to the Pt peak was found allowing all parameters to vary.

2) The parameter of interest was then varied by a small increment from its optimal position.

3) A new "best fit" was found, this time keeping the parameter of interest fixed in its new position.

4) Steps 2 and 3 were repeated three more times giving a total of 5 fits.

5) The five (parameter of interest, X̂) pairs were then least squares fit to a parabola.

6) The variation in the parameter of interest necessary to go from the parabola's minimum to the (minimum+1) was defined as one standard deviation of the parameter of interest.

Table 2.2 shows the results of this procedure for various Pt coverages. All the Pt spectra were taken using the same collection time. Thus, the S/N varies by the square root of the coverage.
TABLE 2.2

<table>
<thead>
<tr>
<th>XML</th>
<th>$\sigma_{\text{mean}}$ (eV)</th>
<th>$\sigma_{\text{FWHM}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>5.0</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>11</td>
<td>0.008</td>
<td>0.03</td>
</tr>
<tr>
<td>54</td>
<td>0.004</td>
<td>0.008</td>
</tr>
<tr>
<td>Bulk</td>
<td>0.002</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Statistical uncertainty in the means of the Pt 4f peak positions and FWHM.

Adding the error due to the peak fitting procedure in quadrature with the uncertainty due to the bin width used during digitization of the data gives an overall error $\leq 0.07$eV. Thus, the spread in data seen in Table 2.1 can not be accounted for by noise. A closer look at this data is warranted.

As outlined in Chapter I, many other workers see coverage dependent shifts in binding energy and peak widths. Substrates including alumina, Teflon, amorphous carbon and graphitic foil all yield these shifts. Table 2.3 lists most of the results for Pt particle size shifts reported in the literature. It should be mentioned that none of these authors actually measured the size of the islands after they were deposited. Except for the authors of reference 32, they all infer island radii from coverage measurements.
TABLE 2.3

<table>
<thead>
<tr>
<th>$\Delta PC^a$ (eV)</th>
<th>$\Delta FWHM^b$ (eV)</th>
<th>Substrate</th>
<th>Theory$^c$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.75</td>
<td></td>
<td>Amorphous C</td>
<td>I</td>
<td>32</td>
</tr>
<tr>
<td>-1.0</td>
<td>-0.51</td>
<td>Graphite Foil</td>
<td>F</td>
<td>5</td>
</tr>
<tr>
<td>-2.5</td>
<td>-0.46</td>
<td>Teflon</td>
<td>I</td>
<td>4</td>
</tr>
<tr>
<td>-1.0</td>
<td></td>
<td>$SiO_2$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>-0.62*</td>
<td>-0.40</td>
<td>$SiO_2$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>-0.3</td>
<td></td>
<td>$\alpha-Al_2O_3[0001]$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>-0.1</td>
<td>-0.1</td>
<td>HOPG(bp)</td>
<td></td>
<td>This Work</td>
</tr>
</tbody>
</table>

$a = (\text{low coverage peak position}) - (\text{high coverage peak position})$

$b = (\text{low coverage FWHM}) - (\text{high coverage FWHM})$

$c = \text{theory to which authors ascribe shifts (I=initial state)}$

F=final state

* This work used mass selected Pt n-mers that varied from 1→6 atoms.

Literature values for shifts in Pt 4f peak positions and FWHM with varying Pt coverage on various substrates.

Table 2.4 contains the data for peak shifts collected in this work. The sample parameters listed in the table are: the Pt coverage after the first deposition, $\Theta_1$, the change in Pt coverage from the first deposition to the last deposition, $\Delta\Theta$, and the time averaged rate at which each of the successive depositions was performed, Evap. Rate. The Pt 4f electrons yield a doublet (4f5/2 and 4f7/2) separated by 3.5eV. This doublet was fit with a pair of Gaussian-Lorentzian curves each having an asymmetric tail. The separation between the curves was fixed at 3.5eV and the percent
Gaussian of each curve was fixed at 80%. In addition, the relative area ratio of the 4f5/2 to the 4f7/2 peaks was fixed at 0.75. The spectral parameters allowed to vary during curve fitting are listed as: the change in the peak center of the fitted curve from the initial deposition to the final deposition, ΔPC, the change in the full width at half maximum of each of the curves used to fit the Pt 4f doublet, ΔFWHM₁ and ΔFWHM₂. FWHM₁ was assigned to the Pt 4f7/2 peak and FWHM₂ was assigned to the Pt 4f5/2 peak. It is clear from Table 2.4 that the Pt/HOPG(bp) system does not show easily interpretable peak shift behavior. Little can be said about comparisons between initial Pt loading, Θ₁, and the size of a subsequent shift upon depositing more Pt. In addition, there appears to be no correlation between evaporation rate and peak shifts in the range 0.01-1 %ML/s. It is striking that all of the peak centers and nine of the ten FWHM show either no shift or a shift toward lower binding energy. It would appear that as more Pt is loaded onto the surface, the Pt 4f peaks shift to lower binding energy and the peaks become narrower.

This effect is small. When all of the data is displayed together, there is no obvious shift with coverage, Figure 2.1. This could be explained by a substrate/island interaction whose energy varies by more than the -0.1eV shift seen when the same substrate is used.
### Table 2.4

<table>
<thead>
<tr>
<th>Run</th>
<th>$\theta_1$ (°ML)</th>
<th>$\Delta \theta$ (°ML)</th>
<th>$\Delta P_C$ (eV)</th>
<th>$\Delta FWHM_1$ (eV)</th>
<th>$\Delta FWHM_2$ (eV)</th>
<th>Evap. Rate (%ML/sec) X 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6</td>
<td>7.3</td>
<td>-0.04</td>
<td>-0.51</td>
<td>-0.57</td>
<td>2.1,2,0.8,66</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>4.1</td>
<td>-0.12</td>
<td>-0.64</td>
<td>-0.23</td>
<td>6.0,4,7</td>
</tr>
<tr>
<td>3</td>
<td>1.3</td>
<td>8.8</td>
<td>-0.22</td>
<td>-0.43</td>
<td>-0.53</td>
<td>13,9</td>
</tr>
<tr>
<td>4</td>
<td>1.9</td>
<td>9.1</td>
<td>-0.03</td>
<td>0.18</td>
<td>0.02</td>
<td>10,46,56</td>
</tr>
<tr>
<td>5</td>
<td>2.3</td>
<td>6.5</td>
<td>-0.07</td>
<td>-0.37</td>
<td>-0.23</td>
<td>23,12,19</td>
</tr>
<tr>
<td>6</td>
<td>5.0</td>
<td>49</td>
<td>-0.04</td>
<td>-0.03</td>
<td>-0.04</td>
<td>5,7,8,10,12</td>
</tr>
<tr>
<td>7</td>
<td>6.2</td>
<td>0.8</td>
<td>-0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>12,12</td>
</tr>
<tr>
<td>8</td>
<td>6.7</td>
<td>7.9</td>
<td>-0.05</td>
<td>-0.27</td>
<td>-0.19</td>
<td>3,8,2</td>
</tr>
<tr>
<td>9</td>
<td>7.6</td>
<td>44</td>
<td>-0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>76,51,120</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>1419</td>
<td>-0.45</td>
<td>-0.55</td>
<td>-0.55</td>
<td>26,33,71,81,1200</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>-0.09</td>
<td>-0.26</td>
<td>-0.23</td>
<td></td>
</tr>
</tbody>
</table>

Shifts in Pt 4f peak positions and FWHM for Pt/HOPG(bp).
Figure 2.1 Pt 4f peak position vs. coverage showing no obvious trend.
2.2 Pt/HOPG(bp) VALENCE BAND

Since most of the discussions of peak shifts in the literature refer to core/valence interactions, it made sense to examine the valence region spectra of the Pt/HOPG(bp) system. Figures 2.2 and 2.3 show the valence band spectra for successively higher coverages of Pt on HOPG(bp). An integrated background subtraction has been performed on each spectrum. Figure 2.2(C) shows that at coverages of 1.5%, a distinct Fermi edge is discernible. Figure 2.3(A) shows that by 10%, the band structure is nearly complete. Figures 2.4(A) and 2.4(B) contain the difference spectra (Figure 2.2B – Figure 2.2A) and (Figure 2.2C – Figure 2.2A) respectively. These difference spectra show that even at coverages as low as 0.6%, a Fermi edge can be found.

Mason et. al use the position of the Fermi edge as an indication of the degree of hybridization of the valence level electrons in Pt islands supported on amorphous carbon.\(^8,^{32}\) Their data shows that in going from \(3 \times 10^{15}\) atoms/cm\(^2\) to \(1.2 \times 10^{16}\) atoms/cm\(^2\), the half maximum point of the edge shifts -0.2eV toward lower binding energy. In addition, they report that the centroid of the valence band shifts by 1.1eV in going from single atoms to bulk Pt. These changes in the valence band region are attributed to increased occupation of d-orbitals using the renormalized-atom theory. A combination of increased coulomb repulsion (between valence d-orbitals and core levels) and decreased final state screening is used to explain the shift in core level binding energy.
Figure 2.2 XPS spectra of the valence band region of Pt/HOPG(bp) at various coverages of Pt: (A) clean HOPG(bp), (B) 0.6% ML Pt, (C) 1.5% ML Pt.
Figure 2.3 XPS spectra of the valence band region of Pt/HOPG(bp) at various coverages of Pt: (A) 10% ML Pt, (B) 55% ML Pt, (C) Pt foil.
Figure 2.4 Difference spectra of the XPS valence band region for low coverage Pt/HOPG(bp): (A) 0.6% ML Pt - clean HOPG(bp), (B) 1.5% ML Pt - clean HOPG(bp).
The Fermi edge and valence band centroid data collected in this work are shown in Table 2.5. The Fermi edge was measured by finding the point in the spectrum that was halfway up the edge. The valence band centroid was found by locating the point through which a line perpendicular to the energy axis bisected the total area under the valence region peak. The ± values for the Fermi edge represent the width of the line in the spectrum. The ± values for the centroid represent the interval over which the bisector could be varied without varying the measured area by more than 1% of the total valence band area. It is clear from this data that there is a shift down in the Fermi edge binding energy on the order of 0.3 eV with a concurrent shift down in the valence band centroid. The shift in the centroid is not quite as large as that reported by Mason et al. This is consistent with the core level binding energy shifts being smaller than those reported by others (see Table 2.3). The shift in the Fermi edge may be the result of a change in the shape of the spectrum as opposed to a change in the Fermi energy itself. One way to test this would be to fit the data to a theoretical curve which contains as one of its parameters the Fermi energy. If it is not possible to fit all the data by changing only the occupancy of different energy levels, then it could be concluded that the Fermi energy does shift.

With this in mind, the question arises as to whether the shape of the valence spectra actually changes in going from 0.7% to 10% Pt or whether the data is of insufficient quality to support such a conclusion. The peak to rms-noise ratio (S/N) of the high binding energy peak of the 10% Pt curve, Figure 2.2(A), is 16. A decrease
TABLE 2.5

<table>
<thead>
<tr>
<th>Coverage (XML)</th>
<th>Fermi Edge (eV) ±0.1</th>
<th>Valence Band Centroid (eV) ±0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>0.2</td>
<td>*</td>
</tr>
<tr>
<td>1.5</td>
<td>0.1</td>
<td>*</td>
</tr>
<tr>
<td>10</td>
<td>-0.2</td>
<td>3.0</td>
</tr>
<tr>
<td>55</td>
<td>-0.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Foil</td>
<td>-0.2</td>
<td>2.6</td>
</tr>
</tbody>
</table>

* These spectra showed a clear Fermi edge but not a clear enough peak structure to measure a centroid.

Fermi edge and valence band centroid of Pt/HOPG(bp).

\[
in \text{Pt to 1.5}\% \text{ would leave } S/N > 6 \text{ (assuming } S/N = (S)^{1/2} \text{). Thus, if the 1.5}\% \text{ and 10}\% \text{ spectra were taken for equal times, a high binding energy peak should be clearly distinguishable. In fact, the 1.5}\% \text{ spectrum was obtained with a 20}\% \text{ longer collection period than the 10}\% \text{ spectrum and still no high binding energy peak is visible. An additional decrease in Pt to 0.7}\% \text{ would decrease } S/N \text{ to 4. Again, with equal collection times, a high binding energy peak should be apparent. In this case, the 0.7}\% \text{ spectrum was obtained with a 650}\% \text{ longer collection period than the 10}\% \text{ spectrum. It can thus be concluded that there is a significant change in the valence band spectrum upon going from 0.7}\% \text{ Pt/HOPG(bp) to 10}\% \text{ Pt/HOPG(bp). It is unclear at this time why the valence band changes so much while the core level peaks display relatively small shifts. It could be}
\]
argued that final state screening is the dominant effect in core level shifts. The π electrons from the HOPG(bp) could provide this screening even for islands without a fully developed valence band thus preventing any large shifts in core level binding energy.

2.3 Heated Pt/HOPG(bp)

The effect of heating the Pt/HOPG(bp) surfaces was assessed by depositing Pt on the HOPG(bp) surface then recording an XPS spectrum. Next the surface was heated until it glowed red (~1000K) and then another spectrum was recorded. Table 2.6 shows the results of these experiments. The parameters in this table are identical to those in Table 2.4 except for Δθ. Here, Δθ corresponds to the change in apparent Pt coverage after heating.

<table>
<thead>
<tr>
<th>Run</th>
<th>Θ₁ (XML)</th>
<th>ΔΘ (XML)</th>
<th>ΔPC (eV)</th>
<th>ΔFWHM₁ (eV)</th>
<th>ΔFWHM₂ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7</td>
<td>-0.1</td>
<td>-0.2</td>
<td>-0.32</td>
<td>-0.17</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>-1.8</td>
<td>-0.12</td>
<td>-0.14</td>
<td>-0.13</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>-3.5</td>
<td>-0.14</td>
<td>-0.11</td>
<td>-0.19</td>
</tr>
<tr>
<td>4</td>
<td>9.8</td>
<td>-4.8</td>
<td>0.06</td>
<td>-0.01</td>
<td>-0.09</td>
</tr>
<tr>
<td>5</td>
<td>14.6</td>
<td>-10</td>
<td>-0.05</td>
<td>-0.03</td>
<td>-0.01</td>
</tr>
<tr>
<td>6</td>
<td>15.7</td>
<td>-6.2</td>
<td>-0.09</td>
<td>-0.13</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

Shifts in Pt 4f peak positions and FWHM of Pt/HOPG(bp) due to heating.
In every case, the Pt/C signal ratio decreased upon heating with an average decrease of 44%. It is possible that Pt has left the surface during heating. Arthur and Cho showed that there is an 80K decrease in the desorption temperature of Cu/C(0001) in going from high to low coverages.\textsuperscript{35} Bulk Pt has a vapor pressure of $1 \times 10^{-9}$ Torr at $-1500K$.\textsuperscript{36} Since during the heating procedure used here the Pt/HOPG(bp) surface does not exceed 1300K, the effect of Arthur and Cho is not likely to be of importance. It is also possible that the Pt has diffused into the graphite; this would be especially likely at defect sites. However, intercalation of graphite is generally carried out at elevated pressure as well as elevated temperature. Thus, it seems unlikely that Pt is finding its way into the HOPG. The most reasonable explanation for the decrease in Pt/C signal ratio is that the Pt islands are reconstructing themselves into three dimensional structures. This would cause much of the Pt to become encased within the islands where its contribution to the XPS signal is attenuated. Neutron activation analysis would be one way to see if the amount of Pt on the surface changes with heating.

As with increasing loading of Pt onto HOPG(bp), it appears that heating the surface causes a slight shift toward lower binding energy and narrower peaks. Unlike the coverage dependent experiments, this data does show a correlation between $\Theta_i$ and the size of the shifts when comparing results of different runs. In particular, the runs with $\Theta_i < 10\%$ show larger shifts than those with $\Theta_i > 10\%$. This is consistent with the valence region results discussed above.
It appears that this system is useful for experimentally probing an ensemble of islands which goes through a 2D→3D transition while keeping the total number of atoms in the ensemble fixed. Surface diffusion of Pt across the HOPG(bp) during heating could cause an increase in island size. In that case, it would not be possible to separate out changes due to island size (ex. 1nm→10nm) from those due to island dimension (ex. 2D→3D). If it is possible to obtain the 2D→3D island reconstruction at a temperature where growth by surface diffusion across the HOPG(bp) is not a dominant effect, these data show that this is a viable system for experimentally separating the electronic effects of the 2D→3D transition with a fixed number of atoms in an island. Angle resolved XPS as well as UHV-STM experiments would help in understanding if this is the case.

In any event, these data clearly show that vapor depositing Pt on HOPG(bp) provides Pt islands that do not behave like bulk Pt and that by sufficient heating or sufficient initial loading of Pt, bulk-like Pt can be formed. In addition, the Pt/HOPG(bp) system is unlike any of those reported in the literature in that the shifts due to increased island size are much smaller than those on any other carbon substrate.

2.4 EFFECT OF AIR EXPOSURE ON Pt/HOPG(bp)

Several of the Pt/HOPG(bp) surfaces were used to examine the effect of exposure to air. It was not possible to fit the oxygen peaks for the air/Pt/HOPG(bp) surfaces using only the peaks listed above in Table 1.2; it was necessary to use a new peak at 531.3eV.
Addition of one new peak was insufficient to obtain a good fit to all of the data. Some of the spectra also showed a new peak at 532.7 eV. Figure 2.5 shows a 5% ML Pt/HOPG(bp) surface which had been exposed to air for >300 hours. The surface displayed a 2% oxygen signal. Figure 2.5(A) shows the oxygen region fit with three peaks. It is obvious that there is a portion of the spectrum not fit by the three peaks obtained from the bare HOPG(bp) curve fits. Figure 2.5(B) shows that the addition of the 531.3 eV peak allows this discrepancy to be removed. Table 2.7 shows the results obtained by fitting the oxygen peaks from six different surfaces exposed to air. The columns labelled %531.3 and %532.7 contain the percentage of the total fitted peak area contained in peaks with these respective positions.

Table 2.7 shows that the amount of oxygen is at least twice that found for a bare HOPG(bp) surface exposed to air for extended periods. As shown by runs two and six, heating reduces the %O to the same level obtained when the bare HOPG(bp) is exposed to air for extended periods. This suggests that the difference in oxygen between heated and unheated surfaces is due to oxygen species associated with the Pt. It is also clear from runs two and six that the 531.3 eV peak area decreases significantly upon heating. Contour et. al have shown that PtO₂ displays an XPS peak at 531.4 eV. This is well within the error of the measurements made in this work. Assignment of the 532.7 eV peak is more ambiguous and will not be attempted.

A controlled experiment was attempted to see if O₂ was responsible for the oxygen signal seen on the air exposed surfaces.
Figure 2.5(A)  O region XPS spectrum of 5% Pt/HOPG(bp) after exposure to air. The spectrum is fit with three curves.
Figure 2.5(B)  O region XPS spectrum of 5% Pt/HOPG(bp) after exposure to air. The spectrum is fit with four curves.
TABLE 2.7

<table>
<thead>
<tr>
<th>Run #</th>
<th>%O</th>
<th>531.3</th>
<th>%</th>
<th>532.7</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>8</td>
<td>3</td>
<td></td>
<td>300 hrs in air + heating (0.9% Pt)</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>14</td>
<td>11</td>
<td></td>
<td>After using STM &gt;100 hrs in air (5% Pt)</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>35</td>
<td>33</td>
<td></td>
<td>~10 min. in air (9% Pt)</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>35</td>
<td>32</td>
<td></td>
<td>~10 min. in air (13% Pt)</td>
</tr>
<tr>
<td>5</td>
<td>0.3</td>
<td>32</td>
<td>8</td>
<td></td>
<td>~10 min. in air (14% Pt)</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>44</td>
<td>16</td>
<td></td>
<td>300 hrs. in air (23% Pt)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>10</td>
<td>26</td>
<td></td>
<td>Heated to red</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>6</td>
<td>61</td>
<td></td>
<td>Heated to orange</td>
</tr>
</tbody>
</table>

0 1S peaks resulting from exposure of Pt/HOPG(bp) to air.

A 60% Pt/HOPG(bp) surface was prepared, transferred into a turbo pumped intro-chamber and then exposed to 10^3L of O_2. Upon transfer back into the UHV chamber, no oxygen signal was detected above the noise. While this would seem to rule out O_2 as the source of the oxygen signal, the following paragraph will show that this is not necessarily the case.

The surfaces exposed to air for only 10 min. (runs 3→5) do not display nearly as much oxygen as those exposed for longer periods. This could be explained by an extremely low sticking coefficient for the oxygen containing species that eventually associates with
the Pt. The section on TPD will deal with this issue further. It is expedient at this time to mention that the TPD results do not indicate a low enough sticking coefficient to explain the phenomena seen here. It is not clear at this time why the oxygen signal is so low for runs 3-5.

Finally, there were no observable changes in the valence band spectra upon exposure to air. Most workers who see changes in the valence band do so using synchrotron radiation.

3 STM

This section is divided into three parts. The first part concerns the bare graphite (0001) surface. A few different surfaces ranging from polished pyrolytic carbon to naturally occurring graphite crystals were examined. The second part includes images and analysis of surfaces that were exposed to Pt vapor in UHV. These surfaces were all examined with either XPS or AES prior to their imaging with the STM. The third section will deal with surfaces that were heated after being exposed to the Pt vapor.

All images were collected in either the topographic mode (constant current=CC) or current imaging mode (CI), with the latter yielding the best atomic resolution. Since the tunneling current varies exponentially with the tip to surface distance, the CI images are displayed as the logarithm of the tunneling current multiplied by a factor which scales the corrugation of clean
graphite to that observed in the CC mode. Even though this
calibration is rather simplistic, images obtained in the CI mode
indicated within a factor of two the same corrugation height found
in the CC mode.

3.1 Graphite (0001)

HOPG ZYB grade crystals were used as substrates for most of
the experiments in this thesis. In order to gain some perspective
on how perfect the HOPG ZYB grade basal plane is with respect to
other graphite surfaces, scans were taken of five different types
of graphite: natural single crystal, HOPG ZYA, HOPG ZYB, HOPG ZYC,
and ordinary pyrolytic graphite (OPG). Figure 3.1(A) shows a
1X1μm² topograph of the natural single crystal surface. The
crystal was a piece of purified Essex graphite. The "three
dimensional photograph" in Figure 3.1(B) is a computer generated
image constructed by assuming a given viewing angle and direction
of lighting. This was the only natural crystal imaged and only a
4μm² area of the surface was examined; thus, any conclusions drawn
from this data should be considered as quite tentative.

3.1.1 NATURAL GRAPHITE

There are several ledges present even on naturally occurring
graphite. "Ledge" will be used to denote the boundary between two
plateaus. It is not intended to imply any relationship between the
periodicity of the nets of the two plateaus. The LEED picture of
this surface showed six very sharp spots and almost no background
intensity. This is consistent with the ledges being steps between
Figure 3.1(A) STM topograph of an Essex natural single crystal graphite (0001) surface.
Figure 3.1(B) 3D computer generated "photograph" of the topograph in Figure 3.1(A).
plateaus with identically oriented nets. As one moves from left to right across this image, each ledge denotes a step down in height. The ledges are all parallel to each other to within ±1°. There are six plateaus in the image; the central four are bounded on two sides by ledges. These central plateaus are integral multiples of 220nm in width. The difference in height between the plateaus is ~0.1nm.

Also apparent in this image is the presence of many dark spots. These circular spots are ~22nm in diameter and ~0.15nm deep. There are 54 spots in this 1μm² area. When imaging a 10X10nm² area around the holes, only a very regular hexagonal pattern of atoms was observed. There was no difference between the images at the center of the hole as opposed to anywhere else on the surface. This same statement can be made of the image taken from a position that straddled a point between the main plateau and the center of the hole. These holes could be due to impurities. An XPS survey scan of the crystal showed only carbon and oxygen. Thus, an impurity theory would have to be based on adsorbates or intercalates containing only these two atomic species. Holes like these were found on a few of the Pt/HOPG(bp) samples. They did not appear on most of the surfaces studied.

Perhaps the most significant aspect of the image in Figure 3.1 is the presence of several bright dots. These objects are very nearly the same size as the Pt islands that will be described below (~5 nm wide and ~0.6 nm high). Thus, impurity effects in STM analysis of metal islands can not be ruled out entirely. However, the object density here is ~10X less than that of the lowest
coverage Pt/HOPG(bp) surface examined. It should be stressed that this author and all of the relevant literature reviewed in this thesis agree on the point that these types of impurities are very rare on HOPG(bp) and, in general, can be ignored.

3.1.2 HOPG ZYB

Figure 3.2 shows a $16\mu m^2$ area of an HOPG ZYB grade surface that had just been cleaved. ZYA grade HOPG gave the same type of image. The difference between ZYA and ZYB is that ZYA has a mosaic spread, $\phi$, of $<0.5^\circ$ while ZYB has a mosaic spread $0.5^\circ \leq \phi \leq 1.0^\circ$. Both grades should have the same quality surface net with a grain size of $\sim 0.5\mu m$. This surface also displays several ledges. The curvature in these ledges is probably due to asymmetries in the X and Y responses of the piezoelectric crystal, an effect which often becomes noticeable in large scans. If one limits the field of view to only $1\mu m^2$ (the size of the image in Figure 3.1), the ledges appear just as straight as those in Figure 3.1. Except for the large ledge in the upper right corner, all the ledges are parallel to within $\pm 1^\circ$. The difference in height between plateaus is $\sim 0.1nm$. The plateau widths, however, are not integer multiples of each other. Most of them vary between 250nm and 300nm with a few plateaus being wider.

This may be related to the fact that the LEED picture of HOPG(bp) ZYA and ZYB surfaces displays multiple spots all at the same radius from the 00 spot. As outlined in the XPS part of this chapter, this indicates that there are several domains with different orientations within the electron beam area. Thus, the
Figure 3.2  STM topograph of a freshly cleaved HOPG ZYB grade (0001) surface.
LEED results imply that at least some of the ledges seen with STM are grain boundaries. However, an average grain boundary spacing of 275 nm would yield >2x10^5 spots in the LEED picture. It is likely that not all of the ledges seen with the STM are grain boundaries. In order to rigorously connect LEED results with STM results, it would be necessary to collect images with atomic resolution on several different plateaus to see if the orientations of the lattices are different. This was not done.

The ledge in the upper right corner of Figure 3.2 is not parallel to the other ledges in the image. It is about 1nm in height, ~10X higher than the other ledges. Most of the ledges seen on surfaces that had been heated in UHV looked like this ledge. The ledges from heated surfaces were often parallel to each other. However, they tended to be spaced further apart than the ledges on this freshly cleaved surface, typically displaying plateaus more than 500nm wide. Based on these STM observations, one might expect the LEED pattern to be different before and after heating. For example, if any of the relevant ledges are grain boundaries, heating should produce fewer spots in the LEED picture. Casual observation of the LEED patterns showed no dramatic change. However, no careful quantitative LEED studies were performed.

As with the natural crystal examined above, this surface also contains a few objects. They are all nearly spherical in shape with radii of ~50nm. This is a size that is much larger than any of the as-deposited Pt islands that will be described below. However, some of the Pt islands on heated surfaces were this large. The object density here is nearly 1,000X less than on the lowest
coverage Pt/HOPG(bp) surface examined. So, again, it is probably reasonable to ignore these types of impurities.

Figure 3.3 shows a highly magnified view of an HOPG(bp) ZYB grade surface. The average spacing between nearest neighbors as determined from a 2D FFT spectral analysis is 0.284nm. Considering the 30% error in the calibration of the piezo scanner discussed below, this is in good agreement with the lattice spacing obtained from X-ray diffraction studies (0.246nm).\textsuperscript{73} The peak to valley height of the imaged atoms is ±0.06nm. This is lower than the 0.09nm value reported by others.\textsuperscript{19} This is probably due to a miscalibration of the z-piezo element. The angle between the primitive vectors describing the surface net in this image is 66°. A perfect graphite (0001) net should display a 60° angle. If one assumes that the HOPG(bp) surface is perfect and that the piezoelectric crystal is accurately calibrated in, say, the X direction, it would require a miscalibration of 30% in the Y direction to account for this difference in angles. The angles measured on other HOPG(bp) surfaces ranged from 59° to 66°. Thus, the miscalibration of the crystal appears to change with time; actually, it is probably temperature and humidity dependent but no log was kept of these parameters.

The way others have dealt with this problem was to assume the HOPG(bp) was a perfect net and then find the mathematical transformation that would take the STM image of the graphite into the perfect net.\textsuperscript{22} This transformation was then applied to the entire image to arrive at the final result. Unfortunately, the miscalibration of the STM used in this work was not detected until
Figure 3.3  STM highly magnified current image of the HOPG ZYB (0001) surface.
after most of the Pt/HOPG(bp) results had been collected. In addition, the Nanoscope II does not contain software to make the necessary transformations. Thus, the length measures of the images presented here contain an unknown lack in accuracy that may be as large as 30%.

3.1.3 HOPG ZYC

Figure 3.4 shows a 25μm² image of an HOPG(bp) ZYC grade surface. This surface should have a mosaic spread at least as good as the ZYB grade surface but should have smaller grain boundaries. The ledges on this surface are certainly not all parallel to each other; although there appear to be two sets of ledges on the left half of the image and, within each set, the ledges are parallel. The height difference between plateaus varies from ~0.5nm to ~2nm. The width of the plateaus varies from ~50nm to ~1000nm. Upon higher magnification, the surface showed a periodic surface net as good as any of the other types of graphite. It would be very interesting to examine this surface with LEED to determine if any of these ledges are grain boundaries. If so, one would expect that the large number of ledges would give rise to many spots in the LEED picture.

3.1.4 OPG

Figure 3.5 shows a 25μm² view of a polished ordinary pyrolytic graphite surface. The exact polishing procedure used is unknown; however, it was probably mechanically polished down to ~1 μm. As a rule of thumb, the rms roughness of a surface is ~0.1 times the
Figure 3.4 STM topograph of an HOPG ZYC grade (0001) surface.
Figure 3.5  STM topograph of an ordinary pyrolytic graphite surface that had been prepared by polishing.
size of the powder used to polish it. In order to measure the roughness, two parameters were obtained, the z-range, $\Delta z$, and the standard deviation in z values, $\sigma_z$. The Nanoscope II software allows the user to define a square box within which these two parameters are measured. In order to minimize the effect of image bowing due to coupling of the z response of the piezo electric element to the X and Y responses, all images were plane subtracted using a second order polynomial. In order to minimize the effect of noise spikes in the measurement, all the images were three point smoothed. Finally, since the natural single crystal image is only $1 \mu m^2$, the larger scans from the other surfaces were measured by defining a $1 \mu m^2$ box size and then taking the average of five measurements equally spaced about the image. Table 3.1 shows the results of these measurements.

### Table 3.1

<table>
<thead>
<tr>
<th>Type of Surface</th>
<th>$\Delta z$ (nm)</th>
<th>$\sigma_z$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPG</td>
<td>140</td>
<td>27</td>
</tr>
<tr>
<td>ZYC</td>
<td>6.6</td>
<td>1.2</td>
</tr>
<tr>
<td>ZYB</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Natural Crystal</td>
<td>0.9</td>
<td>0.15</td>
</tr>
</tbody>
</table>

RMS roughness of various graphite surfaces as determined by STM.

The OPG surface does not show distinct ledges. In fact, it is difficult to find any linear symmetries in this image. The
hillock-like structures in the image have widths ranging from ~100nm to ~1000nm. The OPG did display atomic resolution when examined at high magnification. Thus, all the surfaces are similar at length scales of ≤10nm; the differences begin to appear at ~100nm.

3.2 Pt/HOPG(bp)

After Pt deposition and examination by AES or XPS, the samples were removed from the UHV chamber, left in air for several minutes to several hours in a closed plexiglass container and subsequently transferred to the specimen holder of the microscope. Figure 3.6 shows 0.6X0.6μm² areas of an HOPG(bp) surface before, A, and after, B, deposition of 10% Pt. The image in A was actually obtained from a section of a platinum containing surface which was masked during the deposition process. No evidence for the presence of foreign material could be detected from such unexposed sections, which displayed characteristic HOPG(bp) corrugations at sufficiently high magnification. The 10% Pt specimen, however, was found to contain roughly circular features about 3 to 6 nanometers in diameter. This indicates that the features in Figure 3.6(B) (and subsequent Pt/HOPG(bp) surfaces) are indeed due to Pt deposits on the surface.

3.2.1 Pt/HOPG(bp) AT 300K

Section 3.2.1 will be divided into two sections. First, a brief qualitative overview of the images obtained from Pt/HOPG(bp) surfaces will be given. Second, a statistical analysis of the Pt islands will be presented.
Figure 3.6(A) STM topograph of the masked portion of an HOPG(bp) surface that had a 10% ML Pt spot deposited elsewhere on the surface.
Figure 3.6(B) STM topograph of the 10\% ML Pt spot alluded to in Figure 3.6(A).
Images of 1%, 18% and 40% Pt on HOPG(bp) obtained over a variety of scan sizes are shown in Figures 3.7, 3.8 and 3.9 respectively. The only filtering done to this data was 2nd order plane fitting which subtracts out slight curvatures in the image. The height of the ledges in Figure 3.7(A) is quite small, ranging from -0.05nm to -0.1nm. It is obvious from this image that there is no preferential clustering of islands near ledges. Figure 3.8(A) shows dark spots on the surface as well as bright spots. This is an example of the same phenomenon seen on the natural single crystal graphite described above. The open patch shown in Figure 3.9 was rather unusual. Most of the area examined was similar to the lower left quarter of Figure 3.9.

In order to facilitate a comparison of the differences among these three images, Figure 3.7(B) and 3.8(B) show 100X100nm² areas from the center of Figures 3.7(A) and 3.8(A) respectively. It is visually striking that as the Pt coverage is increased, the number of islands on the surface increases while the size of the islands stays about the same. Assuming two dimensional growth, one might expect that in going from 1% to 18% to 40% the lateral dimension of the islands would increase as the square root of the coverage, i.e. from 1+4+6; this is clearly not happening. In fact, the islands on the 40% surface look like aggregates of the islands on the 1% surface. This assertion will be dealt with more rigorously in the next section.
Figure 3.7(A)  STM topograph of 1% ML Pt/HOPG(bp).
Figure 3.8(A) STM topograph of 18% ML Pt/H0PG(bp).
Figure 3.9  STM topograph of 40% ML Pt/HOPG(bp).
Figure 3.7(B) Central 100X100 nm$^2$ section of Figure 3.7(A)
Figure 3.8(B)  Central 100X100 nm² section of Figure 3.8(A)
Figure 3.10 shows a group of features from a 10% Pt/HOPG(bp) surface consisting of only a few atoms atop of what appears to be a wider island. This is evidenced by the line scan, in which at least two levels of atoms may be identified. Also found in this specimen were loosely associated features consisting of units of atomic dimensions (see Figure 3.11). The exact number of atoms observed in these images may not be determined with certainty because the change in current due to adsorbates is not always a simple step function. This may be attributed to a delocalization of adsorbate charge into the neighboring carbon atoms. Nevertheless, the individual units were reasonably stable surviving several scans.

A close inspection of these images revealed atomic features both in registry and out of registry with the underlying β-sites. In particular, a prominent feature was observed in the scan along the α-sites (see Figure 3.11) with an apparent height measured with respect to the mean graphite corrugation of 0.35nm. In contrast, line scans along the β-sites adjacent to the feature in Figure 3.11 yielded significantly less pronounced changes in the substrate corrugation. This is consistent with the feature being on a bridge β-site and thus in accordance with observations made by Ganz et al. for other metals deposited on HOPG(bp).\textsuperscript{22}

In direct analogy with the results obtained for Ag deposited in UHV and examined in air,\textsuperscript{20} the dimensions of the internal structure of the Pt features observed in this work confirm that adsorbed d-metal atoms can indeed be imaged under ambient conditions. These images are also remarkably similar to those
Figure 3.10  STM topograph of a Small island on a 10% ML Pt/HOPG(bp) surface.
Figure 3.11  STM current image of loosely associated features displaying units of atomic dimension on a 10% ML Pt/HOPG(bp) surface.
reported for Ag, Al, Cu and Au specimens, in which both the
deposition and imaging were performed in UHV.\textsuperscript{22}

Representative areas of 1\%, 18\%, 28\% and 40\% Pt/HOPG(bp)
specimens involving a total of 402 islands were carefully examined
in order to establish correlations between the maximum heights,
$H_{\text{max}}$, of the clusters and the coverage. An F-test analysis of
variance\textsuperscript{76} for $H_{\text{max}}$ of these specimens did not allow for rejection
of the null hypothesis at the 80\% confidence level (i.e. the means
of the heights can not be said to come from different
distributions). As this test does not allow one to draw the
converse conclusion, i.e. that the means are the same at the 80\%
confidence level, a different test was needed. A Student-t test
was used to evaluate the 90\% confidence interval for the data. The
t values were converted to $\pm$ values using

$$
+z = t(\sigma/N^{1/2})
$$

where:
\begin{itemize}
\item $t =$ the 0.05 fractile of the student-t distribution
\item $\sigma =$ the standard deviation of the height values
\item $N =$ the number of islands measured
\end{itemize}

Except for the 18\% surface, all the other surfaces show island
heights that have statistically insignificant differences in their
means. The grand mean (excluding the 18\% sample) is 0.38nm.

The total cluster distribution in terms of $H_{\text{max}}$(ave) is
displayed in the form of a histogram in Figure 3.12. The Pt
covalent bond length is 0.26nm, thus the near complete absence of
islands with heights $>0.5$nm indicates that the distribution of
TABLE 3.2

<table>
<thead>
<tr>
<th>Pt (XML)</th>
<th>No. of Clusters</th>
<th>Mean of $H_{max}$ (nm)</th>
<th>$\sigma$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>0.37 (±0.06)</td>
<td>0.12</td>
</tr>
<tr>
<td>10</td>
<td>51</td>
<td>0.38 (±0.05)</td>
<td>0.23</td>
</tr>
<tr>
<td>18</td>
<td>184</td>
<td>0.31 (±0.03)</td>
<td>0.12</td>
</tr>
<tr>
<td>28</td>
<td>12</td>
<td>0.37 (±0.07)</td>
<td>0.13</td>
</tr>
<tr>
<td>40</td>
<td>143</td>
<td>0.39 (±0.01)</td>
<td>0.01</td>
</tr>
<tr>
<td>1 (heated)</td>
<td>113</td>
<td>7.12 (±0.28)</td>
<td>1.82</td>
</tr>
<tr>
<td>10 (heated)</td>
<td>56</td>
<td>1.70 (±0.16)</td>
<td>0.51</td>
</tr>
</tbody>
</table>

* The heated surface data is included here but will not be discussed until section 3.2.2.

Mean height of Pt islands on HOPG(bp) as measured by STM. islands is two dimensional.

Also analyzed were the average widths, $W_{ave}$, defined as the mean average of the maximum lateral dimension of the cluster along and perpendicular to the scan direction. This data is displayed in Table 3.3.

If one makes the rigorous condition that the island widths must agree within the limits set by the Student-t test, then there is an oscillation in island width with coverage. There is no obvious reason for this to be true. If the data is dealt with less rigorously and it is only required that the mean widths agree to within a standard deviation, then all the coverages except 10% could be said to have the same width islands. This data certainly does not support the theory that island size scales as the square
Figure 3.12  Histogram of Pt island heights
root of the coverage.

<table>
<thead>
<tr>
<th>Pt (%ML)</th>
<th>No. of Islands</th>
<th>Mean of $W_{ave}$ (nm)</th>
<th>$\sigma$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>9.59 (±0.77)</td>
<td>2.21</td>
</tr>
<tr>
<td>10</td>
<td>51</td>
<td>4.68 (±0.40)</td>
<td>1.69</td>
</tr>
<tr>
<td>18</td>
<td>184</td>
<td>12.15 (±1.09)</td>
<td>3.77</td>
</tr>
<tr>
<td>40</td>
<td>143</td>
<td>7.47 (±0.31)</td>
<td>2.17</td>
</tr>
<tr>
<td>1 (heated)</td>
<td>113</td>
<td>77.8 (±2.40)</td>
<td>15.4</td>
</tr>
<tr>
<td>10 (heated)</td>
<td>56</td>
<td>8.62 (±0.39)</td>
<td>3.01</td>
</tr>
</tbody>
</table>

Mean width of Pt islands on HOPG(bp) as measured by STM.

If it is assumed that island width is independent of size, the question arises as to why growth stops at a given size. One possible theory is that smaller islands bind their constituent Pt atoms more tightly than larger islands. There is some support for this in the literature. Kinoshita reviews the effect of particle size on the lattice constant of a particle. In particular, it is found that for several metals, Pt among them, the lattice constant decreases with particle size. This is attributed to surface tension. It is posited that the surface tension grows faster than the particle's internal pressure thus forcing a contraction in the lattice parameter as the particle size shrinks. Calculations of these two energies for various materials indicate that Cu should
show very little contraction with particle size. This is found to be true experimentally. It would be very interesting to carry out experiments similar to the ones done in this thesis using Cu to see if the Cu island size does grow as the square root of the coverage.

There was an attempt made to compare the coverage as measured by XPS with the coverage as measured by STM. The results of this comparison are summarized in Table 3.4 with the following assignments: \( \Theta_{XPS} \) is the coverage as measured by XPS, \( A_{HOPG} \) is the total area over which Pt island sizes were measured, \( A_{Pt} \) is the % of \( A_{HOPG} \) covered by Pt atoms, \( \rho_{Pt} \) is the areal density of islands (i.e. the density of nucleation sites), \( \Theta_{STM} \) is the coverage as measured by XPS. \( \Theta_{STM} \) was calculated with a five step procedure. First, the volume of each island was estimated by multiplying the width along the scan direction by the width perpendicular to the scan direction by the maximum height of the cluster. Second, the number of Pt atoms in this volume was calculated using the atomic radius of Pt (0.139nm) and assuming spherical atoms. Third, the total number of atoms in the analysis area was summed. Fourth, the number of atoms was divided by the area of analysis. And finally, this number was normalized to the cross-sectional area of a single Pt atom assuming a spherical atom.

It is clear from Table 3.4 that even taking into account a 30% inaccuracy factor, there is not good agreement between XPS and STM with respect to coverage measurements. In fact, there appears to be a serious problem in using the technique to measure the volume of small metal islands. As discussed in Chapter I, Ganz et al. had similar problems in trying to measure the volume of single atoms on
the surface. They point out that the tunneling current and bias voltage set points can greatly effect the measurement of adsorbate volumes. The data in this thesis was

<table>
<thead>
<tr>
<th>$\Theta_{\text{exp}}$ (XML)</th>
<th>$A_{\text{HOPG}}$ (nm$^2$)</th>
<th>$A_{\text{Pt}}$</th>
<th>$p_{\text{Pt}}$ (nm$^{-2}$)</th>
<th>$\Theta_{\text{STM}}$ (%ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6x10$^5$</td>
<td>6.6x10$^{-3}$</td>
<td>7.5x10$^{-5}$</td>
<td>1.8x10$^{-2}$</td>
</tr>
<tr>
<td>10</td>
<td>9.0x10$^5$</td>
<td>1.9x10$^{-3}$</td>
<td>1.2x10$^{-4}$</td>
<td>4.0x10$^{-1}$</td>
</tr>
<tr>
<td>18</td>
<td>3.2x10$^5$</td>
<td>1.7x10$^{-2}$</td>
<td>6.1x10$^{-4}$</td>
<td>3.53</td>
</tr>
<tr>
<td>40</td>
<td>1.7x10$^4$</td>
<td>9.1x10$^{-1}$</td>
<td>1.2x10$^{-2}$</td>
<td>197</td>
</tr>
<tr>
<td>1 (hot)</td>
<td>2.5x10$^7$</td>
<td>2.7x10$^{-2}$</td>
<td>4.5x10$^{-6}$</td>
<td>147</td>
</tr>
<tr>
<td>10 (hot)</td>
<td>2.5x10$^5$</td>
<td>1.7x10$^{-2}$</td>
<td>2.2x10$^{-4}$</td>
<td>22.4</td>
</tr>
</tbody>
</table>

Parameters relevant to coverage estimate of Pt/HOPG(bp) using STM.

collected in such a way as to maximize the contrast of the islands. This precluded the use of a single set of tunneling currents and bias voltages. There are relatively consistent trends in the measurements of nucleation site density, $A_{\text{Pt}}$, and area of the HOPG(bp) surface covered with Pt, $p_{\text{Pt}}$.

### 3.2.2 Heated Pt/HOPG(bp)

The work on heated Pt/HOPG(bp) surfaces was done mainly to show that the as-deposited Pt islands were flat. It was thought
that perhaps the as-deposited islands were three dimensional but due to some artifact of the STM, only two dimensional images were being obtained. To this end, the heated experiments were quite successful. As shown in Table 3.2 above, the heights of the heated islands are five to ten times larger than the as-deposited islands. More than ten heated samples varying in coverage from 1% to 70% of a monolayer were spot checked to ensure that this difference in height is generally true. Statistics of island sizes were collected for only two of these, a 1% and a 10% Pt/HOPG(bp) surface (see Tables 3.2-3.4 above).

In general, the large scans (>100nm) looked very much like the unheated surfaces. The main difference was that the islands now appeared to be 5-20 times taller than on the unheated surfaces. In addition, it was not possible to obtain images of these taller islands that displayed atomic scale resolution. The version of the Nanoscope II used in this work is known to have a problem with the current amplifier circuit. The circuit is designed in such a way that the bias voltage applied between the tip and surface is dependent on the tunneling current. This voltage should be independent of the tunneling current. The result is that it is nearly impossible to obtain atomic resolution in scans of bulk metal surfaces. Thus, it is not surprising that different resolution was obtained with 2D as opposed to 3D islands. This problem has been fixed in later versions of the Nanoscope II but none of the data in this work was taken with the updated amplifier.

Figure 3.13 shows a 25µm² view of a surface that showed 0.7% of a monolayer of Pt (as measured by XPS before heating). A double
Figure 3.13 STM topograph of a 0.7% Pt/HOPG(bp) surface which had been heated to ~1000K in UHV.
tip is apparent in this scan, as all islands have a twin just below and to the left. By measuring the distance between the peak of the island and the peak of the twin, it was determined that the two tips were separated by ~120nm. Islands on surfaces offer a system with which tip morphology can be examined much more directly than with single crystal surfaces.

The number and/or size of the islands on this surface is much too large compared with the 0.7% coverage estimate by XPS. There is a factor of 100 difference between the two techniques. There is also a large difference between the widths of the islands on this 1% heated surface compared with the other surfaces (see Table 3.4). This could be explained by one of three theories. First, it is possible that the XPS coverage measurement is very inaccurate. That the XPS measurement is off by ~35% is easily conceivable. However, that it is off by a factor of 100 seems unlikely. Second, it is possible that these are not Pt islands alone being imaged but instead they are islands coated with some contaminant. Air borne proteins or aggregates of smaller hydrocarbons could account for these sizes. The third theory is what might be called a tip amplification effect. If the tip were quite blunt on an atomic scale, then the convolution of the tip shape with the island shape would yield a large island image even if the island itself were small.

There are reasons to discount all of these theories. The first two theories could be discounted by observing that this is the only image in which such well defined large islands were imaged. One would expect that air borne contaminants would appear
in all images. The tip amplification theory can be debunked by pointing out that the ledges in this image are only ~20nm wide, about 3X narrower than the islands. Thus, it remains a mystery as to why these islands appear so large.

Another interesting aspect of Figure 3.13 is the ledge running in a gentle arc across the image. There is no measurable change of height in going from one side of this ledge to the other. When examining the ledge closely, it is found that only the islands are present with no structure in the substrate between them. The other two more linear ledges do show changes in height of ~0.5nm. In addition, they show several islands located along the step edge. This was true of most of the heated surfaces; in contrast to the unheated surfaces, ledges do seem to be preferential sites for islands at high temperature (~1000K). The density of islands along the steps in this image is ~8X10^{-3}nm^{-1}. The density of islands on the plateaus is ~4X10^{-6}nm^{-2}; taking the square root of this to obtain the linear density on the plateaus gives 2X10^{-1}nm^{-1}. Thus the ledge sites appear to be ~4X more favorable toward high temperature growth than the plateau sites. The height of the ledge islands is ~30% lower than the plateau islands and the width of the ledge islands is ~ 20% less.

While the large scans of heated surfaces look, in most respects, like slightly scaled up versions of unheated surfaces, the small scans (~100nm) are qualitatively different. Most of the islands on heated surfaces have smooth boundaries; loosely associated features like those seen in Figure 3.11 are not seen. Figures 3.14 and 3.15 are two of the best examples of island shapes
Figure 3.14  3D island on a heated 1.2% ML Pt/HOPG(bp) surface.
Figure 3.15  Hexagonal 3D islands on a 0.7% ML Pt/HOPG(bp) surface.
seen on the heated surfaces. The approximately rectangular island in Figure 3.14 is very reminiscent of the three dimensional islands seen by Ganz et al.\textsuperscript{22} The structure is roughly 20nm X 24nm X 0.75nm. When trying to zoom in on the surface of islands like these the only obtainable image looks very much like a noise signal. The beautiful hexagonal structures seen in Figure 3.15 are unlike any metal island on graphite STM images published. Using TEM Long et al., however, have seen strikingly similar images of Pt crystallites on amorphous carbon that were aligned but not coalesced.\textsuperscript{61} The individual hexagons have dimensions of 36nm X 41nm X 6.5nm and have sharp vertical edges and flat tops. As discussed in the TPD section, one would expect an FCC metal to nucleate into a shape having square and hexagonal faces. Indeed, the Transmission Electron Microscopy, TEM, literature is filled with images of such nuclei.\textsuperscript{56,57,59,61,62,80}

One might expect that the abundance of "shadows" around the main hexagons was due to a multiple tip effect. However, more than 10 years ago Chu and Ruckenstein saw a nearly identical effect with TEM.\textsuperscript{80} They were looking at Pt vapor deposited on amorphous carbon films at elevated temperatures. They found that when the Pt/C surfaces were heated in 10^{-4} torr of oxygen that both trails and shadows were left on the carbon surface. They hypothesized that trails indicated a normally migrating crystallite whereas shadows indicated a hopping crystallite. They do not give any reasons for why markings are left in the first place. It is possible that the Pt catalyzes the production of CO or CO\textsubscript{2} using the O\textsubscript{2} gas and the C from the substrate. This would leave indentations in the substrate.
as the crystallite effectively "chewed" its way along the surface. However, one would expect that a hopping crystallite would leave behind only outlines of its perimeter and not solid shadows. In any event, if it is the formation of COₓ that causes the markings, then perhaps an analogous reaction is occurring with H₂ in the UHV chamber. It could be envisioned that the Pt crystallites form CH₄ and that this causes depressions in the HOPG(bp). This has been observed previously by Santiesteban et al. using TEM.⁵⁷ Their work was done by exposing the Pt/C to relatively high (~1 torr) pressures of H₂ while the sample was heated. The samples used in this thesis stay at elevated temperatures for >1000s and are exposed to a background H₂ partial pressure in the 10⁻¹⁰ torr range. Assuming that every H₂ that hits the Pt/HOPG(bp) interface reacts, these conditions would be sufficient to account for a noticeable effect on the surface. This hypothesis could be tested fairly easily by dosing the hot sample with H₂ and looking for an increase in the methane signal at the mass spectrometer. A final observation on this topic is that these shadows do not appear consistently on all heated surfaces. They were only seen ~20% of the time.

4 TPD

The previous two sections have shown that the Pt, as deposited, forms two dimensional islands on the HOPG(bp) surface. Upon heating, these islands becomes three dimensional. It has not yet been determined what type of single crystal surface, if any,
these two types of islands resemble with respect to chemical reactivity. This section will show that there is some correlation between the Temperature Programmed Desorption (TPD) spectra of Pt/HOPG(bp) and the TPD spectra of certain single crystal Pt surfaces from the literature. Section 4.1 contains the O/Pt/HOPG(bp) discussion and section 4.2 contains the CO/Pt/HOPG(bp) discussion.

4.1 OXYGEN

Since no quantitative studies were done to determine at what temperature Pt begins to restructure into 3D islands on HOPG(bp), a TPD experiment run entirely below room temperature was the only way to be sure that the same type of unheated islands observed with STM and XPS were being probed with TPD. As pointed out in Chapter I, dioxygen molecularly chemisorbs on Pt well below room temperature. In addition, its desorption peak varies by more than 100K for different Pt surfaces. This allows for O₂ TPD to be used as a relatively non-invasive probe of the the type of crystal face the Pt clusters resemble.

4.1.1 HOPG(bp)

All the TPD experiments were performed in Chamber B (see Chapter II, section 2.2). The first step in these experiments was to record a TPD spectrum for the bare HOPG(bp) surface. A typical spectrum for a surface that was dosed with 20L of O₂ at 100K is shown in Figure 4.1A. The spectrum is flat and featureless over the entire range of interest for molecular O₂ desorption. This
Figure 4.1  TPD spectra of O$_2$ on: (A) bare HOPG, (B) 10% ML Pt/HOPG(bp) as-deposited, (C) 10% Pt/HOPG(bp) after heating to 1000K.
curve shows no evidence of a peak even when it is expanded by a factor of 10. The only data massaging of the curves in Figure 4.1 was to offset them along the pressure axis for ease of viewing.

4.1.2 Pt/HOPG(bp)

Next, spectra were recorded after Pt was deposited on the HOPG(bp). Figure 4.1(b) is a typical spectrum obtained from a $O_2$/Pt/HOPG(bp) surface. There is structure to this curve beyond that expected for the desorption of $O_2$ from a single state. This is evidenced by shoulders both above and below the main peak. However, without a curve fitting analysis it is difficult to determine the position or amplitude of these smaller features. The analysis here will thus be confined to an examination of the main peak only.

In order to determine the amount of Pt on the surface, after TPD the samples were transferred through air into chamber A (see Chapter II, section 2.1) and an XPS spectrum recorded. All of the results reported here are for samples that showed ~10% of a monolayer of Pt. It was only possible to do one run on the flat clusters per Pt deposition because atomically chemisorbed oxygen is left on the surface after heating to room temperature. To clean the surface, it is necessary to heat to ~900K. This heat treatment causes the islands to become three dimensional as shown by STM.
Four spectra from freshly deposited Pt islands were collected with the following results:

\[
\begin{align*}
O_2 \text{ TPD peak} &= 147^{\pm}2(K) \\
O_2 \text{ TPD FWHM} &= 33^{\pm}15(K)
\end{align*}
\]

where the \( \pm \) values are the variances for the data sets. As can be seen from Table 3.1 in Chapter I, the peak positions and FWHM's from the literature are not all in accord with each other for a given surface. Therefore, to compare the values from this work with those in the literature, the averages and variances of the literature data were calculated yielding Table 4.1. The Pt(110), Pt(110)(1x2), foil, and filament surfaces can immediately be ruled out because their peak positions are much higher than the Pt/HOPG(bp) surface. The Pt(111) surface has a consistent peak position, however, the FWHM is significantly narrower than the Pt/HOPG(bp) surface. This leaves both the Pt(100) and Pt(321) surfaces with TPD spectra similar to that of the Pt/HOPG(bp) surface.

Arguments can be made for both of these surfaces. Theoretical calculations by Romanowski,\textsuperscript{24} supported by TEM work\textsuperscript{25,26} show that the equilibrium nucleus for FCC metals is a truncated octahedron (Figure 4.2). (Note: in the literature at least as far back as 1969, this shape is incorrectly referred to as a cuboctahedron: a polyhedron having eight triangular faces and six square faces.) This is one of the 13 Archimedean solids having as faces, six equal squares and eight equal hexagons.\textsuperscript{27} The hexagons would show (111)
# TABLE 4.1

<table>
<thead>
<tr>
<th>Surface</th>
<th>Desorption Peak (K)</th>
<th>FWHM (K)</th>
<th>Heat Rate Rate (K/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(110)</td>
<td>244</td>
<td>51</td>
<td>NA</td>
<td>9</td>
</tr>
<tr>
<td>Pt(110)(1X2)*</td>
<td>200,175</td>
<td>NA</td>
<td>NA</td>
<td>13</td>
</tr>
<tr>
<td>Pt foil</td>
<td>194(±7)</td>
<td>121(±54)</td>
<td>NA</td>
<td>2,3</td>
</tr>
<tr>
<td>Pt filament</td>
<td>180</td>
<td>33</td>
<td>5.6</td>
<td>15</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>150</td>
<td>38</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td>Pt(S)-12(111)X(111)</td>
<td>148</td>
<td>12</td>
<td>4.75</td>
<td>11</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>142(±7)</td>
<td>12(±3.1)</td>
<td>1</td>
<td>6,8,11</td>
</tr>
<tr>
<td>Pt(321)</td>
<td>148</td>
<td>44</td>
<td>10</td>
<td>12</td>
</tr>
</tbody>
</table>

* The Pt(110)(1X2) consists of terraces of Pt(111) faces three atoms wide with monatomic steps and an angle of 109.5° between terraces.

TPD peak positions and FWHM from the literature for O₂ on various Pt surfaces.
Figure 4.2 Line drawings of a cuboctahedron and a truncated octahedron from ref. 27.
character and the squares, (100) character.

Thus, it is possible that the Pt/HOPG(bp) surface has the Pt beginning to form one of the faces of this nucleus. Three dimensional growth is frustrated at room temperature, so the Pt(100) surface just continues to grow on the surface. There is further support for this model in that Wang et al.²⁶ find the (100) face in contact with the substrate when Pt crystallites are grown on SiO₂ and γ-Al₂O₃.

The STM results show Pt that looks more amorphous than crystalline. The Pt(321) surface has the most edges and dangling bonds of any of the surfaces from the literature; thus, it is most likely to display surface chemistry similar to an amorphous surface.

A third argument should be voiced before moving on. There is no reason that the Pt/HOPG(bp) surface must be like a single crystal or any bulk surface. It is possible that these small flat islands have properties that can not be compared consistently with any single bulk surface.

After heating to 1000K there is a significant change in the TPD spectra, Figure 4.1(C). The four surfaces mentioned above were subjected to repeated dosing and heating cycles. Before each dosing, the samples were flashed to 1,000K. In this way, eleven spectra were recorded from surfaces that had been heated one or more times with the following results:

\[ \text{TPD Peak} = 172±5 \]
\[ \text{TPD FWHM} = 17±2. \]

This reflects an increase in peak temperature of 17% and a decrease
in FWHM of 80%. The only peak in the literature this is consistent with is the low temperature component of the doublet from the Pt(110)(1X2) surface reported by Fusy et al.\textsuperscript{13} Fusy attributes the high temperature (200K) peak to O\textsubscript{2} desorbing from step sites and the low temperature (175K) peak is attributed to desorption from the (111) terraces. Thus, it seems that the Pt/HOPG(bp) surface shows Pt(111) character where the (111) surface is in close proximity to a step edge. Since the lower part of the step is carbon instead of Pt, O\textsubscript{2} may be unable to adsorb at the step, thus the 200K peak is absent.

For the particular experiment that yielded Figure 4.1, the heated curve's area is \textasciitilde20\% less than the unheated curve's area. However, this decrease in peak area did not generally hold. There appear to be uncontrolled factors affecting the peak area so no conclusions will be drawn using this parameter.

4.2 CARBON MONOXIDE

The experiments with CO as the adsorbate were performed before the gas doser was calibrated. Thus, dosing was done by backfilling the chamber. Since CO adsorbs strongly on the edge sites of the HOPG crystal, it was necessary to keep the exposure low to minimize the signal from these sites. This constraint makes the comparison of these results to the literature difficult. As explained in Chapter I, the CO TPD spectra are fairly sensitive to the initial coverage of CO. Wherever possible, sticking coefficient vs. coverage curves reported along with TPD results in the literature\textsuperscript{19,22,23} are used to calculate the coverage that should
result on the relevant crystal face from a one Langmuir dose.

4.2.1 HOPG(bp)

As with the oxygen experiments, the first step was to record a background spectrum before depositing Pt, Figure 4.3(A). It is clear that at LL exposure, no effect from the edge sites is seen. Also, there is no evidence of any structure to this background spectrum even when it is expanded by >10X the size shown in Figure 4.3.

4.2.2 Pt/HOPG(bp)

Next, Pt was deposited and an AES spectrum was taken to measure the amount of Pt deposited. Most of the results reported here are for surfaces which showed ~50% of a monolayer of Pt. The STM results indicate that the Pt is two dimensional at these coverages.

Finally, the chamber was backfilled with CO and a TPD spectrum recorded, Figure 4.3(D). Subsequent TPD spectra showed a decrease in the CO peak intensity; TPD spectra were recorded until the CO signal from the dosed surface fell into the background.

In general, the TPD spectra for CO were much more complicated than those for O₂. Several peaks were often observed and the relative intensities of the peaks changed from one run to the next as exemplified by the spectra in Figure 4.3(B-D). The temperature measurements for these experiments were carried out using a thermocouple junction pressed against the front face of the sample. It was difficult, though not impossible, to obtain reproducible
Figure 4.3  TPD spectra for CO on:  (A) bare HOPG,  (B) 50% Pt/HOPG(bp) heated 3X to 1000K,  (C) 50% Pt/HOPG(bp) heated 2X to 1000K,  (D) 50% Pt/HOPG(bp) heated 1X to 1000K.
results with this geometry. However, trends in peak population shifts should not be affected by this problem.

Table 4.3 is a summary of the results from six experiments like those described in the previous four paragraphs. The data is grouped into units consisting of repeated exposure and heating runs on a surface that initially showed a coverage of Pt, θ_{Pt}, by AES. Run 1 represents the spectrum taken from a freshly deposited Pt/HOPG(bp) surface. The data is divided suggestively into three sets of peaks. The average difference between Peak1 and Peak2 is 62(±6)K. The average difference between Peak2 and Peak3 is 49(±5)K. In every case, comparing run #1 with run #3 shows the peak population shifting from a maximum at higher binding energy to a maximum at lower binding energy. By comparing the results from Table 4.3 with those from the literature (see Table 4.4 below) the following observations can be made. Peak1 is consistent with the Pt(110) face. Peak2 is consistent with a 50Å island. Peak3 is consistent only with the low temperature peak from a Pt film.

With the exception of experiment #5, run 1 always displays Peak1; with the exception of experiment #2, run 3 never displays Peak1. This may occur because there is a tightly bound state, similar to a Pt(110) site, available on the 2-D Pt islands that disappears when the islands become 3-D. Or, it is possible that some poisoning effect takes place after the first dosing and heating that blocks the tightly bound states from further activity.

Similarly, with the exception of experiment #2, run 1 never displays Peak3; with the exception of experiment #3, run 3 always shows Peak3. This suggests that there is a loosely bound state,
<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Run</th>
<th>Θ_{Pt}</th>
<th>Peak1 (K)</th>
<th>Peak2 (K)</th>
<th>Peak3 (K)</th>
<th>Peak* Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>Data</td>
<td>not</td>
<td>recorded</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>455</td>
<td>394</td>
<td>0,2,3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>410</td>
<td>382</td>
<td>0,2,3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.8</td>
<td>507</td>
<td>442</td>
<td>412</td>
<td>1,3,2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>470</td>
<td>442</td>
<td>393</td>
<td>1,1,1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>488</td>
<td>434</td>
<td>383</td>
<td>1,2,3</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.5</td>
<td>577</td>
<td></td>
<td></td>
<td>3,0,0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>503</td>
<td>441</td>
<td></td>
<td>3,2,0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>457</td>
<td></td>
<td></td>
<td>0,3,0</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.5</td>
<td>530</td>
<td></td>
<td></td>
<td>3,0,0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td>447</td>
<td>353</td>
<td>0,2,3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>389</td>
<td>0,0,3</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>0.5</td>
<td></td>
<td>463</td>
<td></td>
<td>0,3,0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td>363</td>
<td></td>
<td>0,0,3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td>417</td>
<td>387</td>
<td>0,2,3</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>&lt;0.2</td>
<td>560</td>
<td>461</td>
<td></td>
<td>2,3,0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td>465</td>
<td></td>
<td>0,3,0</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>519(±7)</td>
<td>444(±3)</td>
<td>384(±3)</td>
<td></td>
</tr>
</tbody>
</table>

* This column shows the relative heights for Peak1, Peak2, Peak3 with 3 designating the highest peak and 1 designating the lowest.

Effect of heating on the TPD Peak positions for CO on Pt/HOPG(bp).
<table>
<thead>
<tr>
<th>Surface</th>
<th>Peak (K) Mean</th>
<th>Peak (K) FWHM</th>
<th>Heat (K/s) Rate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>11Å Island</td>
<td>502</td>
<td>150</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>17Å Island</td>
<td>535</td>
<td>100</td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>35Å Island</td>
<td>470,510†</td>
<td>120</td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>40Å Island</td>
<td>428,510</td>
<td>150</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>50Å Island</td>
<td>445</td>
<td>150</td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>70Å Island</td>
<td>398,488</td>
<td>180</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>Film</td>
<td>382,510</td>
<td>196</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>Film</td>
<td>420,510</td>
<td></td>
<td>7</td>
<td>17</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>415</td>
<td>112</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>523</td>
<td>106</td>
<td>4</td>
<td>21</td>
</tr>
<tr>
<td>Pt(321)</td>
<td>428,554</td>
<td>10</td>
<td>50</td>
<td>22</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>552</td>
<td>86</td>
<td>50</td>
<td>23</td>
</tr>
</tbody>
</table>

† Values separated by a "," indicate a doublet in the TPD spectrum.

TPD peak positions from the literature for CO on various Pt surfaces. Only CO coverages relevant to this work are included.
similar to a Pt film, not available in the 2-D islands that comes into existence when the islands become 3-D. Another explanation is that after dosing and heating, a previously passive loosely bound state becomes activated.

If it is assumed that the temperature values obtained in these CO TPD experiments are reasonably accurate, then the following conclusions can be drawn. As deposited, the 2-D Pt behaves like Pt(110). When heated, the Pt clusters behave like a film. There is present in both 2-D and 3-D clusters, a site that behaves like a 50Å cluster.

It is unfortunate that the as-deposited Pt results from O₂ TPD do not agree with those for CO TPD. This prevents one from drawing a simple self-consistent model of Pt island sites based on single crystal faces. However, as pointed out in the introduction, O₂ and CO adsorb onto Pt in very different ways. In particular, adsorbed CO molecules present mutual repulsion which may play a role on a substrate of limited extent that would not be present with adsorbed O₂. Note that Table 4.4 differs from Table 3.3 in Chapter I in that only the peak positions from surfaces with relevant CO coverages have been included.
5 ELECTROCHEMISTRY

The original motivation for the work done in this thesis was to try to understand the particle size effect, (PSE), in electrocatalysis. There has been much work done on this topic but no consensus has been reached as to how fundamental concepts can be applied to explain the effect. The central idea of this thesis was to develop a simple very well characterized model system with which the PSE could be studied. All of the work presented here was related to the characterization of the system. Only the most preliminary studies have been performed using electrochemical techniques. This section will present the results of these experiments.

Two types of experiments were performed both using cyclic voltammetry to probe the Pt/HOPG(bp) surface. The first set of experiments was done in-situ, i.e., the surfaces were not exposed to air between deposition of Pt and formation of the electrochemical cell. The second set of experiments was done in an ex-situ cell designed by Intae Bae.

5.1 In-Situ Electrochemistry

The in-situ experiments were performed in chamber B (See Chapter II, section 2.2). Prior to transferring the samples from the preparation chamber to the electrochemistry chamber, they were exposed to a saturation dosage of CO. It was expected that the CO would protect the surface from undesired contamination during the transfer by blocking the Pt active sites. Once the cell was
formed, the CO was to be removed from the surface by
electrochemical oxidation yielding CO$_2$ which is electrochemically
inert over a wide potential range. Thus, a clean Pt surface would
be left in contact with the electrolyte. This methodology was not
successful in these experiments. In particular, no peak in the CO
oxidation region was found upon the first potential sweep. More
will be said about this in the ex-situ section.

One of the most troublesome problems encountered when doing
electrochemistry on HOPG(bp) is avoiding electrolyte contact with
the edge of the crystal. The interfacial capacity of the edge is
much higher than that of the basal plane. This causes the
electrochemical current contribution from even small areas of the
edge to overwhelm the signal from the basal plane. There are two
ways to overcome this problem. First, the contact area of the
electrolyte can be limited to the basal plane by pressing a
containing vessel firmly against the basal plane. This is how
Bae’s cell is formed. The disadvantage of this design is that, to
get a seal tight enough to avoid any leakage current, the
containment vessel must be pressed against the basal plane hard
enough to cause a macroscopic indentation in the face of the
crystal. This is an inelastic deformation and thus thick pieces of
the crystal must be cleaved after each experiment to obtain a fresh
flat basal plane.

A second procedure for avoiding edge sites is to limit the
extent of the electrolyte itself. This was the procedure used in
the in-situ cell. The separation between counter and reference
electrodes was only ~1mm. Thus, one drop of electrolyte was enough
to bridge both electrodes. The HOPG(bp) could then be brought down from above and as long as the droplet contacted the basal plane more than a few millimeters from the edge, surface tension would confine the contact area to the basal plane.

In order to test the performance of the electrochemical cell before each experiment, a voltammogram using a Ni wire as the working electrode was acquired. Figure 5.1 gives the cyclic voltammogram obtained for the Ni wire exhibiting the characteristic features associated with the oxidation and reduction of the NiOOH/Ni(OH)$_2$ redox couple.

As a means of comparing the voltammetry of Pt/HOPG(bp) with a more conventional Pt system, cyclic voltammetry measurements were conducted with a Pt wire mounted on the same sample specimen holder used with the UHV prepared Pt/HOPG(bp) specimens. The results of this voltammetry are shown in Figure 5.2. As expected the reference potential of the α-Pd-H alloy, as judged by the onset of hydrogen evolution, is 50mV shifted with respect to the reversible hydrogen electrode, RHE, in the same solution. The reference electrode did not always display stable behavior. Occasionally it would drift toward more positive potentials. When this occurred, the onset of hydrogen evolution was defined as -50mV vs. RHE to re-zero the voltammogram. The hydrogen adsorption and desorption peaks on the Pt/HOPG(bp) do not show the distinct doublet nature apparent in Amadelli’s voltammogram (see inset in Figure 5.3). This is probably due to oxygen present in the electrolyte. This hypothesis is supported by the fact that, in the potential range 0.05V to 0.5V, the area between the positive going i-V curve and
Electrode Area = 0.016 cm$^2$
Sweep Rate = 100 mV/s
Electrolyte = 0.1 M KOH

Figure 5.1 Cyclic voltammogram of Ni wire obtained using the in-situ electrochemical cell.
Cyclic voltammogram of Pt wire in 0.1M KOH using the in-situ electrochemical cell.
the line defining zero current is distinctly less than the area between the negative going i-V curve and the zero line. Thus, the hydrogen doublets seen by Amadelli are probably being diffused by a large oxygen reduction current. It should also be noted that the electrolyte in these experiments was not pre-electrolyzed. The only procedure used to obtain clean electrolyte in the vicinity of the double layer was to cycle the potential between 0mv and 1V at 1V/s for ~1 min. just prior to recording the voltammogram.

Figure 5.3 shows the cyclic voltammetry for an 80% Pt/HOPG(bp) sample in 0.1M KOH. The observed features are in fair agreement with those reported earlier by Amadelli shown in the insert for comparison.

One of the most interesting questions yet to be answered about Pt is what mechanism is responsible for the oxide region peaks. Amadelli gives an overview of this subject but it will not be presented here. Angerstein-Kozlowska et al. present a theory in which the Pt goes through a three step oxidation. In that paper, the authors discuss the voltammetry of Pt wires and foils. The Pt surface is divided into two sublattices, Pt(111) and Pt(100). However, the final mechanism used to explain the oxide region of the Pt voltammogram only relies on the Pt(100) sublattice. The first step involves OH⁻ adsorption and takes place in the potential region near -0.4V vs. Hg/HgO. This adsorption takes place until the surface saturates with each OH⁻ anion being 4-fold coordinated with the Pt surface. At this point a place exchange is supposed to take place with Pt-Pt-OH → Pt-OH-Pt. This step is irreversible and corresponds to the anodic going rise in current around -0.15V vs.
Figure 5.3 Cyclic voltammogram of 80% Pt/HOPG(bp) in 0.1M KOH using the in-situ electrochemical cell. Sweep rate = 100mV/s Electrode area = 0.12cm².
Hg/HgO. It is this step that could be studied with the Pt/HOPG(bp) system. The STM results show that at coverages <50%, most of the Pt is only one atom deep; thus, a place exchange should not be possible.

The cyclic voltammetry of a 5% Pt/HOPG(bp) specimen is shown in Figure 5.4. Although the features are not as well defined as in Figure 5.3, clear peaks for hydrogen evolution (~0V), hydrogen adsorption/desorption (~0.2V), oxygen evolution (~1.45V), oxide formation (0.6V~1.3V), and oxide reduction (~0.55V) can be seen at approximately the same positions as those for the much higher Pt loaded specimen. It is interesting that there does seem to be a lack of structure in the oxide region anodic of ~0.56V vs α-Pd. Perhaps this is due to a lack of three dimensionality of the Pt islands. The voltammogram in Figure 5.4 was stable during more than 20 minutes of potential cycling. This provides evidence that relatively small (~5nm diameter) two dimensional Pt islands are stable in alkaline electrolytes and display a voltammetric response comparable in several ways to Pt in bulk form.

5.2 Ex-situ Electrochemistry

The ex-situ electrochemical experiments were performed for three reasons. First, it was desired to examine the voltammetric response of the Pt/HOPG(bp) surfaces in a cell that was known to behave well. Second, the study of CO oxidation on Pt/HOPG(bp) was not possible with the in-situ cell because the CO would discharge the α-Pd-H reference electrode. Third, an experiment in which STM was performed on the Pt/HOPG(bp), followed by cyclic voltammetry,
Figure 5.4: Cyclic voltammogram of 5% Pt/HOPG(bp) in 0.1M KOH using the in-situ electrochemical cell.

Electrode Area = 0.12 cm²
Sweep Rate = 100 mV/s
Electrolyte = 0.1M KOH
then STM again did not require use of the relatively unwieldy in-situ cell.

Figure 5.5 shows the voltammogram of a 10% Pt/HOPG(bp) surface taken in 0.1M HClO₄. The cell was purged with N₂ prior to and during the voltammetry. The slope in the cathodic edge of the scan is an artifact due to the response time of the XY recorder; when slower sweep speeds were used (ex. 100mV/s), the edge was vertical to within ±1mV. The hydrogen adsorption/desorption region of this voltammogram is reminiscent of Pt(111) while the oxide region is reminiscent of Pt(100). The O₂ TPD results also showed that the Pt islands had Pt(100) character. It is possible that the peroxo-like gas phase adsorbed oxygen is behaving similarly to the solution phase adsorbed anion relevant to the oxidation of Pt in HClO₄.

Figure 5.6 shows an 11% Pt/HOPG(bp) surface that had gone through the following sequence of steps after the electrochemical cell was formed. First, the electrolyte was purged with N₂ and a voltammogram was taken that looked very much like Figure 5.5. Next, the electrolyte was purged with CO for 30 minutes while the working electrode was held at OV vs. SCE. Then the solution was purged for 1 hour with N₂. Finally, the voltammogram shown in Figure 5.6 was recorded. The peak at 0.625V vs. SCE appears only on the first sweep and is attributed to CO oxidation. This peak could not be obtained by dosing the Pt/HOPG(bp) surface with 1000L CO in UHV and then transferring the sample through air to the cell.

In order to determine if this effect was unique to Pt/HOPG(bp), the following experiment was performed. A polycrystalline Pt disk electrode was subjected to the same series
Figure 5.5 Cyclic voltammogram of 10% Pt/HOPG(bp) in 0.1M HClO₄ using the ex-situ electrochemical cell.
Figure 5.6

Cyclic voltammogram of 11% Pt/HOPG(b.p.) in 0.1M HClO₄, that had been CO saturated and then flushed with N₂, using the ex-situ electrochemical cell.
of steps described in the previous paragraph. It showed the same voltammetric response with respect to the CO oxidation peak. The crystal was then removed from the electrolyte, dried with a CO gas jet, then immediately replaced in the electrolyte and a voltammogram was recorded. No CO oxidation peak was found. It is thus not surprising that the CO/Pt/HOPG(bp) surface does not survive transfer through air.

The CO oxidation peak was used to titrate the number of sites active for this reaction on the surface. Assuming that two electrons flow for each CO molecule that is oxidized, there were $9.2 \times 10^{13}$ sites/cm$^2$. Using the same 0.139nm radius spherical atom model used in all the other analysis in this thesis, this corresponds to 5.6 %ML. This experiment was repeated on a sample that showed 10% Pt/HOPG(bp) with the result that there were 4.4 %ML active sites. The error in these values due to the area measurement beneath the peak (a planar polarimeter was used for this) is ~7% of the calculated coverage.

The STM/voltammetry/STM experiment was performed only once. Figure 3.8(A) in the section 3.2.1 contains the image obtained before electrochemistry. Figure 5.7 shows the surface after potential cycling between -0.22V and +1V vs. SCE in 0.1M HClO$_4$. Unfortunately, this data was corrupted while it was being saved to magnetic tape. This occurred before any quantitative analysis could be performed. However, it is clear that the density of islands on the surface is about the same and that the islands themselves are approximately the same size. The origin of the striations running through the graphite is uncertain. It is
possible that the basal plane was strained upon formation of the electrochemical cell and that these striations are the result. It is also possible that the HOPG(bp) contains a large degree of stress and that potential cycling allows the surface to relax into a buckled state. Further experiments to show the reproducibility of this effect are in order. It would be logical to start with a bare HOPG(bp) to isolate this effect from anything involving the Pt islands.
Figure 5.7  STM topograph of 18% ML Pt/HOPG(bp) after potential cycling between H₂ evolution and 900mV vs. SCE in N₂ saturated 0.1M HClO₄.
CHAPTER IV

1 CONCLUSIONS

1. XPS shows that the "atomically perfect" HOPG(bp) net which STM users refer to possesses 100 to 1000 times more defect sites than are accounted for by STM and LEED results.

2. The defects shown by STM are ledges, however, no preferential nucleation of metal islands is seen at these ledges at 300K. This suggests that there may be active sites for nucleation on HOPG(bp) that are not seen by STM or that nucleation occurs simply by Pt atoms finding each other on the surface.

3. It is possible to image d-metal islands with STM. In addition, atomic resolution within the islands is possible. This is the first time this has been done.

4. Vapor deposition of Pt on HOPG(bp) at 300K forms two dimensional islands that are only one or two atom layers high. This thesis presents the first statistical analysis showing this fact using STM.

5. Individual Pt atoms seem to prefer β sites and β-β bridge sites on the HOPG(bp) surface.
6. STM shows that Pt islands do not preferentially nucleate at ledge sites on HOPG(bp) at 300K.

7. Islands do seem to preferentially nucleate at ledge sites at elevated temperatures (~1000K).

8. It is non-trivial to compare STM in air with XPS in making coverage estimates. The reason for this is not known. There is an increase in object density with coverage that STM is sensitive to. This indicates that one method of Pt island nucleation is by Pt atoms finding each other on the surface and not by a single Pt atom finding a pinning site on the substrate.

9. Pt island growth at 300K does not proceed by unbounded increase in previously existing nucleation sites. Instead, more nucleation sites are formed with increasing coverage.

10. The decrease in binding energy, ~0.1eV, and FWHM, (~0.3eV), of the Pt 4f XPS line with Pt coverage is smaller than that seen by others on various carbon substrates. The lack of a large shift is explained by the STM results. Even at coverages as low as 1% ML, the Pt forms islands with several hundred atoms in them. Thus, bulk electronic properties should be expected.
11. Heating Pt/HOPG(bp) causes the XPS Pt/C signal ratio to decrease by ~40%. STM shows that heating causes a 2D→3D transition of the Pt islands. This may indicate that the decrease in the Pt XPS signal is due to Pt surface atoms becoming internal bulk Pt atoms in a 3D island. This is the first time a 2D→3D transition has been observed with STM.

12. Heating Pt/HOPG(bp) also causes a decrease in the Pt 4f binding energy, 0.1 eV, and FWHM, 0.1 eV.

13. XPS shows Pt/HOPG(bp) adsorbs oxygen when exposed to air for periods much longer than 10 minutes. In addition, heating to 1000K removes this oxygen. The XPS spectra show that at least PtO₂ is formed. Another unidentified oxygen species is also present.

14. O₂ TPD on Pt/HOPG(bp) has been reported for the first time. There is a 25K increase in the O₂ TPD peak (from 147K → 172K) which occurs when the surface is pre-heated to 1000K. This indicates that while XPS shows only a small change in the electronic structure between as-deposited and heated Pt/HOPG(bp), TPD indicates a large change.
15. TPD of CO on Pt/HOPG(bp) has also been reported for the first time. There is a shift in the TPD peak with heating. In this case, however, the shift is up in temperature instead of down. In addition, the shift is much smaller with respect to the FWHM of the peak than in the O₂ case.

16. Coverage estimates based on CO oxidation in HClO₄ agree with XPS estimates to within a factor of two.

17. Pt/HOPG(bp) at coverages <10% ML displays distinctly different voltammetry in KOH than bulk Pt. At coverages between 50% and 100% ML, the Pt/HOPG(bp) voltammetry appears similar to the bulk Pt.

2 FUTURE WORK

1. Use a vibrational spectroscopy such as HREELS or FTIR to identify the type of oxygen on the air exposed HOPG(bp) and Pt/HOPG(bp) surfaces.

2. Determine whether the low energy peaks in the AES spectrum of HOPG(bp) are diffraction peaks by heating the surface >2000K.
3. Use angle resolved XPS to look for differences between the 2D and 3D island electronic structure.

4. Look for a shift in the Fermi energy of Pt islands with island size by fitting the XPS data to an analytic function that contains as one of its parameters the Fermi energy.

6. Look for surface tension effects in metal island growth on HOPG(bp) by using Cu. One would expect to find a square root relationship between Cu coverage and island radius if surface tension is playing a dominant role in fixing the size of metal islands.

7. Look for post-reaction signs of catalysis with the STM by dosing a hot Pt/HOPG(bp) surface with H₂ and then looking for etch marks with the STM. Compare these results with SEM data for surfaces that had been treated thoroughly enough to create etch marks large enough to view with SEM.
BIBLIOGRAPHY

PREFACE REFERENCES


SUBSTRATE PREPARATION AND ISLAND FORMATION REFERENCES


167


XPS REFERENCES


13. Dr. Walter Lambrecht, Private Communication.


31. Dr. Intae Bae, Private Communication.


34. Professor D. Keith Robinson, Private Communication.


STM REFERENCES


3. J.K Trolan, U.S. patent No. 2 786 955.


18. M.P. Green, K.J. Hanson, D.A. Scherson, X. Xing, M. Richter, P.N. Ross, R. Carr, I. Lindau, "In Situ Scanning Tunneling Microscopy Studies of the Underpotential Deposition of Lead on Au(111)," The Journal of Physical Chemistry, 93 no. 6, (1989) 2181-2183.


37. R. Gomer, R. Wortman, R. Lundy, Journal of Chemical Physics, 26, (1957) 1147.


42. Dr. Eric Ganz, Private Communication.


71. All the graphite, except the OPG, was obtained as a gift from Arthur Moore at Union Carbide.

72. Dr. Arthur Moore, Private Communication.


TPD REFERENCES


ELECTROCHEMISTRY REFERENCES

1. Amadelli, (Ph.D. Dissertation, Case Western Reserve University, 1982).