Infrared reflection-absorption spectroscopy of thin film structures

Steven James Finke
Iowa State University
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Infrared reflection-absorption spectroscopy of thin film structures

Finke, Steven James, Ph.D.
Iowa State University, 1988
Infrared reflection-absorption spectroscopy
of thin film structures

by

Steven James Finke

A Dissertation Submitted to the
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Signature was redacted for privacy.
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For the Major Department
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For the Graduate College

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# TABLE OF CONTENTS

1 INTRODUCTION .................................................. 1

2 LITERATURE REVIEW ........................................... 3
   2.1 Vibrational Spectroscopy of Surfaces .................... 3
   2.2 PM-FTIRRAS ............................................... 4
      2.2.1 Theory .............................................. 4
      2.2.2 Applications of the technique ...................... 16
   2.3 Optical Properties of Thin Film Structures ............ 31
      2.3.1 Equations for reflections at interfaces .......... 32
      2.3.2 Reflections at air/metal interfaces ............... 34
      2.3.3 Optics of multilayer films ....................... 35

3 PM-FTIRRAS SPECTROMETER DESIGN ......................... 40
   3.1 FTIR Spectrometer ........................................ 40
      3.1.1 Standard features ................................ 40
   3.2 Modifications for PM-FTIRRAS .......................... 46
      3.2.1 Optics ............................................. 46
      3.2.2 Signal handling electronics ...................... 48
   3.3 PM-FTIRRAS Cell .......................................... 58
   3.4 Gas Feed System .......................................... 60
4 EXPERIMENTAL PROCEDURE

4.1 PM-FTIRRAS System Operation and Optimization

4.1.1 FTIR operation and parameter settings

4.1.2 Optimization of the PM-FTIRRAS system

4.2 Thin Film Preparation

5 EXPERIMENTAL RESULTS

5.1 Theoretical Justification

5.2 Analysis of Thin Film Structures

5.3 PM-FTIRRAS of Thin Film Structures

5.3.1 PMMA/silicon/copper systems

5.4 Palladium Thin Films

5.4.1 Palladium thin film deposition processes

5.4.2 Palladium thin films from palladium acetate

5.4.3 IRRAS of palladium acetate decomposition

5.5 Thin Catalyst Films

5.5.1 Molybdenum trioxide thin films

6 CONCLUSIONS AND RECOMMENDATIONS

7 BIBLIOGRAPHY

8 ACKNOWLEDGEMENTS

9 APPENDIX: PM-FTIRRAS circuit diagram
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Illustration of the phase change of polarized light upon reflection from a metal surface</td>
<td>6</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Illustration of the optimization of the angle of reflection and the sample size</td>
<td>8</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Absorption coefficients for a thin film of acetone on silver</td>
<td>9</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>IRRAS spectra of NO adsorbed on platinum foil under various pressures of NO gas</td>
<td>14</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>IRRAS spectra of six L-B monolayers of cadmium arachidate on silver: a) single beam spectrum, b) ratioed spectrum</td>
<td>17</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>Absorption band for CO adsorbed on a platinum surface for various sample pretreatment: a) fully annealed and cleaned, b) partially cleaned</td>
<td>19</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>Illustration of the Langmuir-Blodgett monolayer deposition process</td>
<td>29</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>Notation used in the reflection equations</td>
<td>33</td>
</tr>
<tr>
<td>Figure 2.9</td>
<td>Variation of the complex refractive index through the 1732 cm⁻¹ absorption band of PMMA</td>
<td>36</td>
</tr>
<tr>
<td>Figure 2.10</td>
<td>Calculated values of the absorption coefficient of CO on several Pd/Si substrates</td>
<td>39</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Diagram of the optical layout of a Nicolet 60SX Fourier transform infrared spectrometer</td>
<td>42</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Optical layout for the PM-FTIRRAS experiments</td>
<td>47</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>PM-FTIRRAS signal demodulation circuit</td>
<td>49</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>Detector signal as a function of frequency during modulated experiments</td>
<td>51</td>
</tr>
</tbody>
</table>
Figure 3.5: Examples of interferograms from several optical systems: a) output of the lock-in amplifier, b) low pass filter output, c) combined interferogram from the switch circuit .......................... 53

Figure 3.6: Fortran program used to split an interferogram data file into two files containing even and odd numbered data points .......................... 55

Figure 3.7: IRRAS spectra of adsorbed CO on palladium using several different optical set-ups: a) static polarizer, b) modulation spectrum, c) modulation with KBr plate compensation .......................... 57

Figure 3.8: PM-FTIRRAS cell used in the reflection studies .......................... 59

Figure 3.9: Diagram of the gas feed system used with the PM-FTIRRAS system ........................................................................................................... 61

Figure 4.1: Illustration of the phase adjustment between the reference and sample signals ........................................................................................................... 66

Figure 5.1: Theoretical calculations for the mean square electric field strength as a function of polarization and distance above the interface ........................................................................................................... 71

Figure 5.2: Schematic diagram of the variables effecting the magnitude of the electric field at a reflecting surface ........................................................................................................... 73

Figure 5.3: Linear approximation equations for the calculation of the effect of a thin film on reflectivities ........................................................................................................... 76

Figure 5.4: X-ray diffraction patterns of thin film structures of copper and silicon: a) silicon/copper thin film structure, b) 1200 Å copper film ........................................................................................................... 79

Figure 5.5: Auger depth profile of an evaporated copper film on a Pyrex cover glass ........................................................................................................... 81

Figure 5.6: Auger depth profile of an evaporated thin film structure of silicon/copper ........................................................................................................... 82

Figure 5.7: Transmission infrared spectrum of PMMA ........................................................................................................... 85

Figure 5.8: Transmission infrared spectrum of an 800 Å film of PMMA on a silicon wafer ........................................................................................................... 87

Figure 5.9: PM-FTIRRAS spectra of an 800 Å film of PMMA on silicon: a) difference spectrum, b) PMMA on silicon, c) silicon wafer reference ........................................................................................................... 88
Figure 5.10: PM-FTIRRAS spectra of: a) a 200 Å film of PMMA on a copper substrate, b) copper substrate .......................... 90

Figure 5.11: PM-FTIRRAS spectra of: a) a 800 Å thick film of PMMA on a copper substrate, b) copper substrate ......................... 91

Figure 5.12: PM-FTIRRAS spectra of: a) a 200 Å film of PMMA on a Si/Cu thin film structure, b) Si/Cu substrate ...................... 92

Figure 5.13: PM-FTIRRAS spectra of: a) an 800 Å film of PMMA on a Si/Cu thin film structure, b) Si/Cu thin film structure .......... 93

Figure 5.14: PM-FTIRRAS spectra of PMMA films of various thickness on a Si/Cu thin film structure: a) 250, b) 80, c) 22 angstroms, d) Si/Cu substrate ........................................ 95

Figure 5.15: Structure of palladium acetate trimer .......................... 99

Figure 5.16: Transmission infrared spectra of palladium acetate: a) thick film from a chloroform solution, b) KBr pellet sample ... 101

Figure 5.17: PM-FTIRRAS spectrum of: a) palladium acetate film on copper, b) bare copper film ................................. 103

Figure 5.18: PM-FTIRRAS spectra of: a) palladium acetate on a silicon/copper thin film structure, b) thin film structure ......... 104

Figure 5.19: PM-FTIRRAS spectrum of: a) thick film of palladium acetate on a silicon/copper substrate, b) silicon/copper substrate ........................................ 106

Figure 5.20: PM-FTIRRAS spectra of: a) very thin film of palladium acetate on a silicon/copper substrate, b) silicon/copper substrate ........................................ 107

Figure 5.21: Decomposition of PdAc/Cu in 10% O₂/He at 100 °C: a) initial spectrum, b) after 1 hour, c) 2 hours .................... 108

Figure 5.22: Decomposition of PdAc/Cu in 10% O₂/He at 100 °C (cont.): a) 2.5 hours, b) 4 hours, c) 5 hours ......................... 109

Figure 5.23: Decomposition of PdAc/Cu in 10% H₂/He at room temperature: a) initial spectrum, b) after 30 minutes, c) 60 minutes ........................................ 111
Figure 5.24: Decomposition of PdAc/Si/Cu in 10% O₂/He: a) initial spectrum at 100°C, b) 123°C, c) 145°C, d) 145°C for 20 minutes

Figure 5.25: Decomposition of PdAc/Si/Cu in 10% H₂/He: a) initial spectrum, b) after 12 hours at room temperature, c) at 75 °C

Figure 5.26: PM-FTIRRAS spectra of a 200 Å molybdenum trioxide film on palladium: a) 300 °C in O₂/He, b) 200, c) as-deposited

Figure 5.27: PM-FTIRRAS spectra of an evaporated MoO₃ film at 300 °C in 10% O₂/He: a) 10 minutes, b) 30 minutes

Figure 5.28: PM-FTIRRAS spectra of molybdenum trioxide/palladium thin film structures in the presence of 1,3-butadiene vapor at the following temperatures (°C): a) 100, b) 200, c) 300, d) 350

Figure 5.29: PM-FTIRRAS spectra during oxygen flow over hydrocarbon treated MoO₃ thin film structure: a) annealed film, b) initial film

Figure 5.30: PM-FTIRRAS spectra: a) during the combined flow of oxygen and butadiene over MoO₃/Pd at 300°C, b) initial film

Figure 5.31: PM-FTIRRAS spectra of: a) maleic anhydride on MoO₃/Pd thin film structure, b) initial substrate

Figure 5.32: PM-FTIRRAS spectra of maleic anhydride on a molybdenum trioxide/palladium thin film structure as a result of purging with helium: a) purging for 2 minutes, b) 20 minutes

Figure 5.33: PM-FTIRRAS spectra of: a) γ-butyrolactone on a MoO₃/Pd thin film structure, b) substrate

Figure 5.34: Comparison of spectra for liquid (a), vapor (b), and condensed (c) butyrolactone on MoO₃ thin film structure

Figure 5.35: Comparison of spectra for solid (a), vapor (b), and condensed (c) maleic anhydride on MoO₃ thin film structure
LIST OF TABLES

Table 3.1: Symbols used in schematic of FTIR optical components ... 43
Table 3.2: Table of values for the cutoff frequencies of the standard filters in the signal path of the 60SX FTIR ... 45
Table 4.1: 60SX FTIR parameter settings for PM-FTIRRAS spectrometer ... 64
Table 5.1: Results of the reflection equations for thin film structures for variable angle of incidence ... 74
Table 5.2: Results of the reflection equations for thin film structures for variable film refractive index ... 74
Table 5.3: Results of the linear expansion theory for thin film structures for variable angle of incidence ... 77
Table 5.4: Results of the linear expansion theory for thin film structures for variable film absorption coefficient ... 77
Table 5.5: Resulting film thicknesses for films spun from several concentrations of PMMA in chloroform ... 86
Table 5.6: Infrared band assignments for the palladium acetate ... 102
1 INTRODUCTION

In the last ten years there has been a remarkable trend in research toward gaining an understanding of the surface phenomena that affect many important processes. Processes that have been used with success for years have been subject to renewed scrutiny with respect to the role that surface phenomena play in the chain of events. As a result of this emphasis, there has been much progress in the ability to study surfaces at the exclusion of the bulk material. Several industries rely heavily on the ability to analyze surfaces.

Microelectronics and catalysis are two such fields. The majority of microelectronic fabrication processes involve interfaces and surfaces that, in many cases, react quite differently from the bulk materials. In addition, these surface phenomena play an important role in the characteristics of the reaction process and the final products. Surface science provides the means of understanding these processes in order to handle the ever increasingly difficult requirements of highly competitive markets. In catalysis, knowledge of both the product distribution and the presence of adsorbed reaction intermediates as functions of reaction conditions is routinely acquired.

The work outlined in this dissertation has contributed to the exploration of new methods of investigating thin films and surfaces in order to understand and control the fundamental processes involved. Optical spectroscopy has played an important role in research, with more and more detailed information coming into
the realm of possibility every day. With its ability to examine reacting systems nondestructively, optical spectroscopy has contributed heavily to the understanding of these processes. As an example of optical spectroscopy, infrared spectroscopy has been used for many years to characterize the types of chemical bonds present. Recently, modifications to standard IR techniques have increased its surface sensitivity by many orders of magnitude. Infrared reflection-absorption spectroscopy (IRRAS) has been used to characterize single crystal metal surfaces during many adsorption processes, and has contributed heavily to the fundamental understanding.

In this work, the useful range of systems on which IRRAS can be used has been extended to systems of thin film structures of semiconductor and catalytic materials.
2 LITERATURE REVIEW

2.1 Vibrational Spectroscopy of Surfaces

Surface science techniques can be split into several groups depending on how the exciting energy interacts with the sample and what type of detector is used. The exciting energy as well as the detected signal can be in the form of electromagnetic radiation or particles [1]. Surface microscopy and diffraction techniques involving electrons provide information about the surface structure and include such techniques as scanning electron microscopy (SEM), and high and low energy electron diffraction (HEED and LEED). Electron beams can also be used to eject detectable core electrons of the surface atoms. Auger electron spectroscopy (AES) yields surface composition information. Other techniques use different exciting beams to initiate the same process, for example the technique of X-ray photoelectron spectroscopy (XPS). The analysis of ejected ions or molecules can also be used to characterize the types of adsorbed molecules on a sample surface in addition to the surface composition. Such techniques as ion scattering spectroscopy (ISS) and secondary ion mass spectroscopy (SIMS) fall into this category. The use of thermal energy to desorb molecules is a common technique known as temperature programmed desorption (TPD).

Nondestructive surface-sensitive techniques have been developed that use lower energy exciting beams. The two techniques most commonly available for the
study of the bonding of adsorbed molecules to surfaces are electron energy loss spectroscopy (EELS) and infrared reflection-absorption spectroscopy (IRRAS).

In many respects, the two techniques are similar, and in reading the literature dealing with the investigation of chemical bonding to surfaces, an understanding of both techniques is essential. The techniques differ in the sample environment during the analysis and the resolution of the spectral information (see for example [2]-[5]). For the study of reacting systems of molecules and surfaces, IRRAS conditions more closely replicate the actual conditions under which reactions take place.

Although infrared spectroscopy has been used extensively for the study of gas/solid adsorption and reaction processes, many samples (e.g. low surface area and samples that absorb strongly in the IR) have remained uncharacterized. The goal of this research was the investigation of the reaction processes on semiconductor and catalyst surfaces using infrared reflection-absorption spectroscopy. A specific sample configuration (referred to here as thin film structures) was developed in order to allow the study of these processes under in situ conditions. The work outlined in this dissertation was performed using infrared reflection-absorption spectroscopy in order to carry out in situ analyses of catalytic reactions and thin film depositions.

2.2 PM-FTIRRAS

2.2.1 Theory

Infrared reflection-absorption spectroscopy (IRRAS) is a surface sensitive spectroscopic technique capable of obtaining spectra of submonolayer coverages of species adsorbed on single crystal metal surfaces in the presence of an absorbing
gas. The theory is based on the physics of the reflection of light from a smooth metal surface (for further reference on optical theory see Born and Wolf [6] or Heavens [7]). Upon reflection, the electric field vector of light undergoes a phase change, the magnitude of which depends on the plane of polarization of the incident light. Figure 2.1 defines the nomenclature to be used in this dissertation. The electric field vector of light polarized perpendicular to the plane of incidence (Is) shifts by 180 degrees, and the shift is independent of the value of the angle of incidence. A node exists in the electric field at the surface due to the destructive interference of the incident and reflected light. Light polarized parallel to the plane of incidence (Ip) undergoes an electric field shift of up to 90 degrees depending on the actual incident angle. The normal components of the incident and reflected rays interfere constructively, and an oscillating electric field exists at the surface in the normal direction. As a result, samples on the surface that have vibrational modes normal to the surface absorb Ip preferentially. This small difference in absorption is the basis for reflection-absorption spectroscopy.

2.2.1.1 Development and improvements The application of this theory to thin films was first investigated by Greenler [8]. It was found that the angle of incidence that resulted in the maximum absorbance of Ip by a thin film was 88 degrees as measured from the surface normal. Below this angle, the normal components of the reflected beam became increasingly smaller so that the enhancement of the electric field decreases. This angle, however, was experimentally difficult to achieve due to the divergence of the infrared beam. Rabolt et al. [9] have since demonstrated that the optimal angle for the reflection is a compromise between the optimal values for enhancement of the electric field and the “illumination factor” for the sample. The theoretically calculated best
Figure 2.1: Illustration of the phase change of polarized light upon reflection from a metal surface
angle for the reflection was found to be near 92 degrees. These results are shown in Figure 2.2. As shown in the figure, grazing angles above the optimal value result in increased amounts of the infrared beam bypassing the sample surface. Using the equation

$$ p = \frac{w}{\cos \Theta}, \quad (2.1) $$

the percentage of the beam that strikes the surface is given by

$$ \% \text{ beam illuminating the surface} = \frac{w \times l}{w \times p} = \frac{l \times \cos \Theta}{w}, \quad (2.2) $$

where \( w \) is the diameter of the infrared beam, \( p \) is the illuminated length of the sample, \( l \) is the total length of the sample, and \( \Theta \) is the angle of incidence measured from the surface normal. Below the optimal value of the reflection angle, less of the sample surface is illuminated by the infrared beam, calculated similarly as:

$$ \% \text{ sample illuminated} = \frac{w \times p}{w \times l} = \frac{w}{l \times \cos \Theta}, \quad (2.3) $$

The optimal value for the reflection angle is the angle at which both these quantities are maximized, or the angle at which the entire length of the sample is illuminated by the infrared beam with none of the beam bypassing the sample:

$$ \frac{w}{l \times \cos \Theta} = 1 \quad \text{or} \quad \cos \Theta = \frac{w}{l} \quad (2.4) $$

The actual value of the absorption factor is a combination of this illumination factor and the reflective characteristics of the metal substrate. As mentioned earlier, the maximum in the absorption factor for \( Ip \) was found to be 88 degrees as shown in Figure 2.3 with the absorption factor for \( Is \) several orders of magnitude smaller. Further, Greenler investigated the effects of film thickness and refractive index on the absorption. He reported that the magnitude of the
Figure 2.2: Illustration of the optimization of the angle of reflection and the sample size
Figure 2.3: Absorption coefficients for a thin film of acetone on silver
absorption varied approximately linearly with the value of d/λ (the film thickness to wavelength ratio) up to values of about 0.0004. His results suggested that Ip could be used to study thin films on metal surfaces. In a later paper, Greenler [10] reported values of the absorption factor as functions of the angle of incidence and the number of reflections from the sample surface. It was found that, in some cases, the absorption factor could be increased by using the optimal reflection angle and several reflections from the surface. In most cases, it was found that the overall signal-to-noise ratio was maximized by between 2 and 8 reflections from the surface. By taking into account the "illumination factor" and the increased complexity of the cell design for multiple reflections, a single reflection was found to be close to optimal. In a later paper, Greenler [11] reported reflectivity values for 19 different metals and concluded that a single reflection resulted in ΔR values of greater than 70 percent of the maximum for 15 of the metals.

2.2.1.2 Modulation techniques Large increases in the sensitivity of this infrared technique were obtained by the addition of modulation techniques to the basic electric field enhancement described in the previous section. Standard transmission infrared spectroscopy is hindered by several phenomena that lower the ability to observe surface species. Among these are strong absorptions by the gas phase ambient around the sample surface as well as the spectrometer optics and sample emissions in the infrared region due to a heated sample. The relative numbers of adsorbed and gas phase molecules can be adjusted by purging the ambient with nonabsorbing gases, evacuating the space around the sample, or increasing the surface area of the substrate by dispersing it on a very high surface area support material. As a result, spectra of adsorbed molecules could routinely be collected.
In situ studies of single crystal surfaces require the ability to differentiate between the sample and effects of the ambient phase and sample emission. The basis for modulation techniques is the ability to modulate between two different optical configurations: one which allows information about the sample and the undesirable phenomena to reach the detector, and another which allows only the information about the phenomena to reach the detector. The detector signal is then demodulated into the two different configurations and the results are subtracted. The result is an enhancement of the information about the sample at the expense of the phenomena that are taking place around the sample. This demodulation is accomplished by phase-sensitive detection which compares the detector signals due to the two optical configurations and outputs a quantity that is proportional to the differences in the two signals.

There are many examples of modulation techniques throughout the ellipsometry and spectroscopy literature but the underlying processes are basically the same. In the next sections the details of the application of modulation techniques to infrared reflection-absorption spectroscopy will be discussed.

In these sections, the use of the word “sensitivity” implies the ability of the particular optical system to discriminate between the absorptions by the sample and the phenomena described earlier. Hence, low sensitivity implies the technique or system does not discriminate between the sample and the optical phenomena, the result being spectra that are more difficult to interpret due to the presence of features that are due to both sample absorptions and the other phenomena. High sensitivity indicates that the resulting spectra show features that are due predominantly to the sample with little or no interference from optical effects of the spectrometer system, sample emissions, or strongly absorbing gas phase molecules in the optical system or the sample ambient.
Several modifications were made to the first basic designs of IRRAS spectrometers in order to increase the sensitivity of the technique. Modulation techniques were added to the system in order to obtain spectra which discriminated between adsorbed species and signals due to sample emission, absorptions by the spectrometer, and absorptions by gas phase molecules. Blanke et al. [12] and Krebs and Luth [13] placed a rotating-blade chopper in the infrared beam between the source and the sample in order to eliminate sample emission. The detected intensity modulated between two values: one containing the sample absorptions as well as the “unwanted” emission (chopper open), the other containing the information about the sample emission only (chopper closed). The signal at the detector was then demodulated by a lock-in amplifier tuned to the frequency of the chopper. The output from the lock-in was proportional to the difference in the two intensities, and this difference was monitored while scanning the wavelength range of interest. The result was a spectrum of the sample without the interference from sample emissions.

Another modulation technique reported by Hoffmann and Bradshaw [14,15] made use of the difference in the sample’s ability to absorb the Is and Ip polarized beams. In this technique, a rotating polarizer was placed in the infrared beam between the source and sample. The rotating polarizer rapidly alternated the polarization of the light from parallel to perpendicular to the plane of incidence at the sample. The detector signal was demodulated and the ratio of Ip to Is was output to the recorder. The spectrometer and the randomly oriented gas phase molecules absorbed Ip and Is equally; hence, the ratio (Ip/Is) eliminated these contributions to the spectra.

Both modulation techniques were used simultaneously by Golden et al. [16]. The sensitivity of the technique was again improved by the modification of the
signal demodulation scheme. The intensity difference ($I_p - I_s$) and the intensity sum ($I_p + I_s$) were sent simultaneously to an analog ratiometer and the result was sent to the recorder. They published the spectra shown in Figure 2.4 of NO adsorbed on platinum foil under various partial pressures of NO vapor. Absorptions due to atmospheric water vapor are absent even though two meters of the beam path was through ordinary room air.

### 2.2.1.3 Fourier transform spectroscopy

Before the late 1970s, most infrared spectrometers were dispersive types, using slits to determine spectral resolution and scanning the wavelength range of interest while measuring the intensity of the infrared beam. Benziger et al. [17] have recently published a review of dispersive infrared reflection-absorption spectroscopy.

The availability of Fourier transform infrared spectrometers with their inherent advantages (Griffiths [18]) increased greatly in the late 1970s. Golden et al. [19] have published a comparison of Fourier transform and dispersive spectroscopy for use with IRRAS.

There are several important advantages in using FTIR for this technique. They include the increased light throughput in FTIR due to the lack of slits in the beam path, the ability to co-add many scans in order to increase the signal-to-noise ratio, and the precise peak calibration due to the use of a laser as a reference. The combination of FTIR and the double-modulation techniques greatly increased the signal-to-noise ratio of the reflection spectra. The interferometer in the FTIR effectively modulates the intensity of the infrared beam in much the same way as the light chopper in dispersive systems. The frequencies of modulation depend on the wavelength of light and the mirror velocity of the interferometer. These frequencies, sometimes referred to as the
Figure 2.4: IRRAS spectra of NO adsorbed on platinum foil under various pressures of NO gas
Fourier frequencies, are defined as

\[ f_F = 2vV \quad (2.5) \]

where \( v \) is the frequency of light in wavenumbers, and \( V \) is the mirror velocity; they range from 10-10,000 Hz in normal FTIR operation. The first reports of the use of modulation techniques in combination with FTIR appeared in the literature in 1979 (Dowrey and Marcott [20], Nafie and Deim [21], and Nafie et al. [22]). Although not in relation to reflection spectroscopy, their work in circular dichroism, with its simple translation to linear dichroism, developed much of the theory of polarization modulation FT-IRRAS.

Golden and Saperstein [23] reported the use of FT-IRRAS to study cadmium arachidate films on silver substrates. The polarization of the infrared beam was modulated by a fixed polarizer combined with a zinc selenide photoelastic modulator (PEM). A good review on the theory of operation of photoelastic modulators was given by Drake [24]. A PEM consists of a transparent crystal that is stressed along one of its principal axes at a high frequency (\( > 10^4 \) hertz). As a result, the plane of polarization of an incoming beam is shifted by 90 degrees (half-wave retardation). This polarizer/PEM combination replaced the rotating polarizer used in previous work and has several major advantages. There are fewer moving parts in the system that wear and add vibration noise to the spectra. The modulation rate is also much higher with the PEM, in the 40-100 kHz range compared to 10-20 kHz for rotating polarizers. This higher frequency is necessary because the signal demodulation circuit requires that the modulation rate differ from the Fourier frequencies by several orders of magnitude. With this large difference, electronic filters can be used to filter out the standard Fourier frequencies that would otherwise saturate the lock-in amplifier. Figure 2.5a shows
the single beam spectrum of six cadmium arachidate layers on a silver substrate. The entire beam path was open to atmospheric air causing the large absorbance due to carbon dioxide and water vapor. Figure 2.5b shows the ratioed spectrum of the same six monolayers.

The most recent improvements to the system have involved the use of a tunable diode laser as the source of infrared radiation (Butler et al. [25], Bermudez et al. [26] and Sass et al. [27]). The more intense beam produced by the laser was found to increase the signal-to-noise ratio. However, the spectral range was limited, and the complexity of the experimental apparatus was greatly increased.

2.2.2 Applications of the technique

The technique has been used to study a variety of thin films and adsorbed gas molecules. A good review of the published results for a variety of substrates and adsorbates is given by Darville [28]. By far the most often used substrate for the technique has been metal surfaces, either single crystals or polycrystalline films deposited on a flat substrate. The sensitivity of the technique depends on the reflectivity of the substrate and varies as a function of the refractive index and the film thickness (Greenler [11]). The most commonly used metals have been Pt, Pd, Ni, Cu, and Ag. These metals exhibit the largest reflectivity values in the infrared range. As a result, the electric field generated at the surface is large. Work has been performed on such surfaces as W, Cr, and Ru although the reflective characteristics of these metals result in less sensitivity to the adsorbed species. Several reports of IRRAS experiments on semiconductor surfaces have appeared in the literature. The results for these studies and the interpretation of the results will be reviewed in a later section.
Figure 2.5: IRRAS spectra of six L-B monolayers of cadmium arachidate on silver: a) single beam spectrum, b) ratioed spectrum
2.2.2.1 Ultra-high vacuum techniques  The published experimental results using IRRAS have been divided into two categories in this review. The first category contains experiments performed in ultra-high vacuum chambers that produce nearly "ideal" surfaces in terms of surface cleanliness and the concentration of defects in the crystal structure. IRRAS has been used on these surfaces to obtain information on the mechanisms that are involved in gas-solid reactions. Typical results include information on the type of molecules present on the surface and their interactions with both their neighbors and the substrate itself. Theories on the processes of adsorption, reaction, and desorption have been developed by combining IRRAS with other techniques such as temperature-programmed desorption (TPD). The details of the reported work in which IRRAS was used are summarized here.

Carbon monoxide has been by far the most commonly studied adsorbate due to its relatively strong interactions with a variety of metal surfaces and its intense absorption bands in the infrared region near 2000 cm\(^{-1}\) (see for example Figure 2.6 from Golden [29]). Since the investigations by Eischens et al. [30] in which transmission infrared spectroscopy was used to study the interaction of CO with supported metal catalysts, many studies have been initiated in an effort to characterize CO/metal systems. Only recently, with the development of infrared reflection-absorption spectroscopy, has the study of single crystal metal surfaces been possible. A more detailed look at the CO/Pt system illustrates the wealth of information provided by this technique.

Shigeishi and King [31] were one of the first groups to study the bonding of CO to the Pt(111) surface as a function of CO exposure and substrate temperature using infrared reflection-absorption spectroscopy. In an effort to simplify the interpretation of the results and obtain information about the catalytic activity of
Figure 2.6: Absorption band for CO adsorbed on a platinum surface for various sample pretreatment: a) fully annealed and cleaned, b) partially cleaned
individual crystal faces, single crystals of metals were used in conjunction with ultra-high vacuum techniques. An unexplained shift in the adsorption frequency with increasing coverage was noted in the early studies. Several hypotheses were under consideration as the reason for the shift; either there was a change in the chemical nature of the CO/metal bonding as the coverage changed, or there were coverage dependent interactions between the adsorbed molecules. The apparent half-width of the infrared band near 2100 cm$^{-1}$ was monitored during the shift as an indication of changes in the bond character between the CO and the metal. No change in the half-width indicated that the actual cause of the shift was the interaction between the adsorbed molecules themselves. In a later paper (Crossley and King [32]), isotopic labeling was used to describe further the dipole-dipole interactions between the molecules as a function of coverage.

Krebs and Luth [13] studied the adsorption of CO on Pt surfaces using a double beam infrared technique which allowed more sensitive analysis of the system. LEED patterns indicated that the CO overlayer structure changed as a function of the surface coverage with more molecules adsorbing at bridge sites at higher coverages. With the added sensitivity of the double beam spectrometer, a second band was observed near 1872 cm$^{-1}$ and was assigned to CO molecules adsorbed in bridging positions between two platinum atoms. The presence of the band along with the linear band near 2050 cm$^{-1}$ indicated that the adsorption process took place sequentially, filling the "on top" sites first then shifting to a combination of "on top" and bridging sites as the surface coverage increased.

Studies of other crystal faces were performed in order to clarify differences in the reactivity and adsorption characteristics ([33]-[36]). Strong dipole coupling was observed using isotopic labeling studies, indicating that the adsorption process is an island growth process.
Low temperature adsorptions were performed in order to determine the change in infrared spectrum as a function of the ordering of the adlayer (as determined by LEED) [34,37,38]. An additional band was seen near 1810 cm\(^{-1}\) for adsorption temperatures above 130 K. This band was assigned to CO molecules adsorbed in 3-fold coordination. This band was present only in combination with the band at 1850 cm\(^{-1}\) indicating that the 3-fold sites were filled as a result of disorder in the adlayer due to crowding of the molecules.

The high resolution of the infrared reflection technique was used to find previously hidden features in the bands for the linearly bonded CO ([39]-[41]). A doublet in the region above 2000 cm\(^{-1}\) was assigned to two-phase adsorption at temperatures below 160 K. Two infrared bands were isolated; one in the range of 2065-2078 cm\(^{-1}\) and the other in the 2086-2097 range [34]. More studies were performed using more complex platinum surfaces in order to model the catalyst particles present on supported metals [34] more closely. The (553) face used in these studies can be described by alternating terraces and steps with an average terrace width of 4 atoms and monatomic steps. The infrared spectra taken as a function of coverage indicated that the lower wavenumber band appeared first and was due to adsorption on the step sites of the surface. As the coverage increased, the higher wavenumber band appeared, indicating the filling in of the terrace sites. No bridge-bonded molecules were observed on that surface. The results were interpreted in terms of a change in the dipole-dipole interactions resulting from 1-D and 2-D arrays of adsorbed molecules. Evidence for three adsorption sites on faces, edges, and corners of crystal planes were presented later (Greenler et al. [41]). Additional evidence of the presence of multiple bands in the linear region has been attributed to adsorption of the CO on defect sites in the platinum surface that change the bonding structure [42].
The high sensitivity and resolution of IRRAS were also used in the analysis of the integrated band intensity of the linear bonded molecules for the (110) surface. Hayden et al. [43] noted a maximum in the band intensity versus coverage for adsorption at 300 K. The decrease in intensity at higher coverages was interpreted as a tilting of the C-O axis of the linearly bonded molecules as a result of crowding on the surface.

The co-adsorption and reaction of several gases on platinum surfaces has also been studied using infrared reflection-absorption spectroscopy. The reaction of CO and oxygen in the presence of a platinum surface has been studied by several groups [44]-[48]. It was discovered that the infrared band at 1875 cm$^{-1}$ disappeared first as the oxidation took place, indicating that the bridge-bonded species were the first to react and leave the surface as CO$_2$ [45]. In addition, no shift in the band positions were evident which indicated that oxidation took place at the edge of CO islands on the surface [46]. It was also noted that the oxidation reaction was inhibited by complete coverage of carbon monoxide. This result suggested that Langmuir-Hinshelwood mechanisms were operative for this system. For the condition of preadsorbed oxygen, the bands shifted as a function of the reaction progress indicating that Rideal mechanisms were in effect.

Several other studies in which reactions of CO and molecules such as water [49] and NO [50] on platinum surfaces have appeared in the literature.

The previous pages have described in detail the information that has been added to the understanding of the adsorption and reaction of CO on platinum surfaces by the use of external reflection infrared spectroscopy.

The same types of studies have been performed on a variety of chemical systems that are important in the understanding of catalytic systems. The reaction of CO on copper films and crystals has been studied in detail [51]-[63]. It
was found that the shift in frequency of the absorption band due to adsorbed CO was much smaller (2 cm$^{-1}$) than that for the CO/Pt system. Through the use of isotopic labeling and surface potential measurements, it was determined that the lack of shift in the absorption band was due to offsetting effects of a large positive shift due to dipole-dipole interactions and a large negative shift due to changes in the chemical nature of the bond to the copper surface. Most recently, Hoffmann and Paul [64,65] have studied the adsorption of CO on copper that was dispersed on a ruthenium substrate.

The CO/Ni system has been studied by a variety of workers [66]-[72] with the result that small dipole-dipole shifts were noted as a function of the coverage of the CO adlayer. The bands were shown to shift as the type of adsorption changed, starting with a band near 1820 cm$^{-1}$ at low coverage (< 0.05 monolayers), shifting to 1910 cm$^{-1}$ near 0.5 monolayers, and finally to 2045 cm$^{-1}$ for saturation coverage. The shape of the absorption band has been studied in detail [68]-[70] in order to infer structural changes in the ordering of the adsorbed layer as the coverage changed.

IRRAS has been used to investigate the effect of the presence of alkali metals on transmission metal surfaces on the adsorption and reaction of CO [73]-[76]. A series of papers ([74]-[76]) has described the effects of potassium on the surface of nickel. Large shifts in the vibrational frequency of the adsorbed CO occurred as the potassium coverage was increased. By varying the relative coverages, two types of interactions were hypothesized: 1) long range interactions were indicated by the inability of nickel to adsorb CO even for very low coverages of potassium, and 2) short range interactions evident by new vibrational modes of CO molecules adsorbed near potassium atoms with the band position of the distant molecules unchanged. Further work [66] used isotopic labeling to investigate the mechanism
of C-O bond scission by examining the reaction:

\[ ^{13}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O} \rightarrow ^{13}\text{C}^{18}\text{O} + ^{12}\text{C}^{16}\text{O} \] (2.6)

It was found that the potassium promoted the decomposition of the CO into adsorbed carbon and oxygen which desorbed in the statistical ratio of the isotopes. As a result, the "feeder site" mechanism was proposed in which the dissociated carbon and oxygen were transferred to the adjacent nickel sites by surface diffusion.

Other studies of CO adsorption on Pd [15], [77]-[79], Ru [80]-[82], Ag [83], Au [84], Ir [85,86], Rh [87], and W [88,89] have been performed using the high resolution and sensitivity of IRRAS to investigate the adsorption and reaction processes of these surfaces.

The adsorption of nitric oxide on transition metal surfaces has been a topic of interest due to its "similarity" to carbon monoxide as a comparative study and the implications of the adsorption and reaction of NO on transition metal surfaces to the pollution control process. Several studies of the process have used IRRAS to monitor the adsorption surface [50],[90]-[94]. Early reports suggested that NO adsorbed to form dimer complexes on metal surfaces [90], but later studies using isotopic labeling concluded that dipole-dipole shifts were present in the system and that there was no evidence for dimer formation. NO adsorbs similarly to CO with bands near 1400 cm\(^{-1}\) due to bridge-bonded molecules and bands near 1750 cm\(^{-1}\) due to the linearly adsorbed molecules. Dipole-dipole interactions cause wavenumber shifts of up to 35 cm\(^{-1}\) as a function of coverage depending on the metal substrate.

The adsorption of other gases such as NH\(_3\) [95], H\(_2\)O [49],[96]-[101], have been studied using reflection-absorption infrared spectroscopy and are only
Small hydrocarbon molecules have also been studied on a variety of surfaces in order to obtain information on the types of intermediates formed as a result of the adsorption of the molecules. In addition, the orientation of the molecules relative to the surface has been determined. This information has a direct bearing on the catalytic processes that take place on metal sites of many catalysts. Hydrocarbons containing nitrogen [102]-[107] have been studied on a variety of surfaces in order to determine the orientation of the C-N bonds relative to the surface.

Due to the wide use of methanol as a feed stock for the synthesis of larger hydrocarbon molecules, the study of the adsorption and reaction of methanol on many metal surfaces has also been studied [108]-[111]. Oxides of molybdenum have been used as catalysts for many reactions involving the oxidation of hydrocarbons. Infrared reflection-absorption spectroscopy has been used to study thin films of MoO$_3$ on metal substrates in the presence of gas phase methanol vapor [108,109].

The adsorption of formic acid on copper surfaces has also been studied using reflection-absorption infrared spectroscopy. Several workers [112]-[116] have used formic acid and labeled molecules to investigate the formation of formate species on the surface and, using the surface selection rules for metal systems, explored the orientation of the formate with respect to the surface. It was found that for low temperature adsorptions (100 K) the formic acid adsorbed molecularly and formed multilayers with a high level of hydrogen bonding as indicated by the width of the absorption bands. Above 270 K the acid decomposed to form surface formate groups in either monodentate or bidentate configurations, as indicated by the presence or absence of the infrared band near 1650 cm$^{-1}$, which was indicative of the asymmetric COO vibration. In addition, the presence of a
combination band was discovered [115]. This band was assigned to two vibrational modes, both having dipole shifts parallel to the surface. Separately, these individual bands would not appear in the surface infrared spectra due to the strict surface selection rules in effect. In combination, however, the band appeared.

The adsorption of other molecules including ethane [117], ethylene [118,119], acetic acid [120]-[122], cyclohexane [123], and thiophene [124] has been studied using reflection-absorption spectroscopy. Malik et al. [119] used the formation of ethylidyne species on the platinum surface to verify the surface selection rules in the surface infrared spectroscopy. It was noted that only three of the six fundamental vibrational frequencies appeared in the infrared spectra, even though all six appeared in spectra of platinum supported on alumina. The strict adherence of the molecular vibrations to the selection rules supported the use of IRRAS in the determination of the orientation of adsorbed molecules. Acetic acid was found to form acetate species on a slightly oxidized metal surface of copper, whereas acetate and methyl groups were noted on nickel surfaces along with acid dimers for low temperature adsorptions. The ring structures of both the cyclohexane and thiophene were determined to be parallel to the metal surface due to the lack of ring-breathing vibrational modes in the surface infrared spectra.

As improvements were made to the optical and electronic components of the infrared spectrometers, the sensitivity of the technique was increased and smaller molecules with much less intense absorptions in the infrared region were studied. The interaction of diatomic gases with metal surfaces has been studied using the combination of IRRAS and LEED in order to determine changes in the bond strengths as a function of the coverage and the amount of order in the adsorbate layer. H₂ [125]-[132], O₂ [137], [132]-[134], and N₂ [136,138] adsorption processes have also been reported.
Canning and Chesters [137] used IRRAS to investigate the low temperature adsorption of oxygen on platinum. The spectra collected at 80 K in the presence of $^{16}$O and mixtures of $^{16}$O and $^{18}$O indicated that, under these conditions, oxygen was adsorbed molecularly. The positions of the bands and the shifts were then used to model the dipole-dipole interactions of the adsorbed molecules.

A study by Brubaker and Trenary [138] involved the adsorption of N$_2$ on the Ni(110) surface. At low crystal temperatures, three distinct vibrational modes were observed. In addition, the expected shift in the band position with increasing coverage was not present. By using other analysis techniques, it was concluded that the changing chemistry between the adsorbate and the nickel surface offset the changes due to dipole-dipole interactions, and that the three different vibrational modes were due to molecules adsorbed in different environments (e.g., the edge of a nitrogen "island" as opposed to the middle of an island).

2.2.2.2 Electrolyte solutions  Another application of IRRAS has been the study of adsorbed species present at interfaces between electrodes and electrolyte solutions. The technique works equally well for liquid/solid interfaces as for gas/solid interfaces, although most liquid cells incorporate very small gaps between the electrode and the window to reduce the strong absorptions due to the liquid layer (Datta et al. [139]). Typical data reported from such experiments consist of IRRAS spectra as functions of the electrode potential. Severson et al. [140] used the technique to investigate CO adsorption on a platinum electrode in a sulfuric acid solution. It was found that the effective coupling of the vibrations of the adsorbed molecules was twice as great as the coupling observed under UHV conditions. A good review of the technique of IRRAS as applied to electrode systems was given by Pons et al. [141].
2.2.2.3 Thick film structures The second major category of applications of IRRAS is that of multilayer or thick films of materials on metal surfaces. These experiments are performed generally under atmospheric pressure conditions, often in sample holders with no temperature or pressure control. The object of the experiments is to determine the types of interactions between the film and the substrate and the orientation of the molecules in the films relative to the surface. A review of the uses of IRRAS for thick film structures has been published by Swalen and Rabolt [142].

The most commonly studied samples in this category have been multilayer films of long-chain aliphatic acids or acid salts known as Langmuir-Blodgett (LB) monolayers. The films were named after Langmuir [143] and Blodgett [144], the original researchers of the technique of building the layers. Monolayers of the acids were deposited by repeatedly dipping a glass slide in a tank of water on the surface of which was dispersed a monolayer of the acid. Blodgett claimed that as many as 200 monolayers could be built up one-by-one so that films of various thickness could easily be prepared and studied. The technique was remarkable in that the films were highly oriented with alternating layers of "head-up" and "head-down" molecules as shown in Figure 2.7 (from Peterson and Girling [145]). Since that time, several other classes of compounds have been deposited using the Langmuir-Blodgett technique, and the usefulness of the films has spread into the semiconductor industry in the form of both conducting and insulating thin films (Peterson and Girling [145] and Roberts [146]). These highly ordered, variable-thickness films were used extensively in the development of the IRRAS technique.

The most commonly studied molecule in LB films has been cadmium arachidate (CdAA, (Cd(OOC-C_{18}H_{36}-CH_{3})_{2}). IRRAS has been used to study
Figure 2.7: Illustration of the Langmuir-Blodgett monolayer deposition process
the orientation of the aliphatic chains by noting differences in the relative intensities of the absorption bands in the spectra as a function of the type of deposition method, reaction with other molecules such as water, and degree of heating and cooling of the film [147]-[156]. The double-modulation technique was used by Golden et al. [19] to clarify structural differences between layers of CdAA on aluminum deposited by the LB method and layers deposited by solution-absorption techniques. Differences in the relative intensities of the absorption bands indicated that the long aliphatic chains were oriented more closely to the normal direction in the LB films than they were in the solution-absorption films. It was also found that the intensities of the absorption bands is approximately linear with the number of layers in the film. Long-chain aliphatic acids have been studied [157]-[160] with the conclusion that the aliphatic tails of the acid molecules are oriented nearly normal to the metal surface and the acid group interacts with the metal.

Thick films of other molecules have been considered in addition to LB films [161]-[188]. The interaction of polymers with metal surfaces has been a topic of much concern in recent years. As a result, IRRAS has been used to study the interface between the polymer and metal in order to determine the extent of interaction and the effects of the surface on the properties of the polymer [161]-[175]. Schlotter and Rabolt [176] developed a temperature controlled grazing incidence reflection (GIR) infrared cell to study the molecular orientation in the films as a function of the film temperature. Thin films (< 500 Å) of poly(methyl methacrylate) (PMMA) supported on evaporated silver films changed orientation as the glass transition temperature (Tg) was approached. No changes were observed below Tg, indicating that very thin films acted much like the bulk polymer. In addition, IRRAS has been used to investigate the interaction of other
large molecules and thick films with metal surfaces that are important in the areas of biology \[181,182\], adhesives \[183\]-\[186\], and corrosion protection \[187,188\].

The studies mentioned in the previous pages indicate that infrared reflection-absorption spectroscopy is a useful tool in the investigation of molecular adsorption, reaction, and orientation on metal substrates. The technique has developed into an important tool for producing high-resolution spectroscopic information under the conditions of pressure and temperature applicable to important catalytic surface reactions. It has been shown to be sensitive enough to analyze monolayer coverages and provide valuable information complementary to other surface sensitive techniques such as EELS and TPD. The development of this technique has been one of the first steps in bridging the gap between the "ideal surfaces" in ultra-high vacuum technology and the real world of catalysis and other chemical reaction processes.

The work described in this dissertation has been a contribution to the next step in the development of IRRAS; the application of the technique to reactions on a variety of new surfaces that are as yet uncharacterized.

\[2.3\] Optical Properties of Thin Film Structures

Infrared reflection-absorption spectroscopy has been used nearly exclusively for the case of adsorbates or films on metal surfaces. The technique is based on the physics of the reflection of light from a smooth metal surface, the topic of many textbooks and articles in the area of ellipsometry.

It is well established that the reflected light differs in both intensity and phase relative to the incident light. The magnitude of these differences depends on several characteristics of the system: the polarization state of the incident light,
the angle of incidence relative to the surface normal, and the refractive indices of the reflecting surface. In ellipsometry, the goal is the determination of the complex refractive index of the reflecting surface by the measurement of the characteristics of the reflected beam. The values of the indices can then be used to characterize the electric field vectors at any point in the light beam for a variety of reflection geometries. These values are published in many reference books and are easily obtained (see for example [189]).

The refractive index of a material is a numerical representation of the ability of the material to transmit electromagnetic radiation. The index is generally written in terms of an imaginary number of the form \( n - ik \). The value of \( n \) is representative of the speed of electromagnetic radiation in the material relative to its speed in a vacuum. The value of \( k \) is representative of the absorption of the light by the material. For transparent (nonabsorbing) materials, \( k = 0 \) and the refractive index is real.

For the simplest systems, numerical equations have been developed that describe the reflected light in terms of the refractive indices of the surface involved. Several of these equations will be reviewed here. This information will be used in the theoretical analysis of the thin film structures in order to verify their potential in external reflection spectroscopy.

2.3.1 Equations for reflections at interfaces

The equations that follow refer to Figure 2.8. The equations are used to calculate the amplitudes of the reflected and transmitted rays for both components of polarization [7]. Reflection at a transparent material is the simplest system to solve numerically. The components of the reflected beam, described in
Figure 2.8: Notation used in the reflection equations
terms of the incident beam as

\[ r = \frac{E_0^-}{E_0^+} \quad \text{and} \quad t = \frac{E_1^+}{E_0^+}, \quad (2.7) \]

can be determined by solving the equations:

\[ r_{1p} = \frac{n_0 \cos \Theta_1 - n_1 \cos \Theta_0}{n_0 \cos \Theta_1 + n_1 \cos \Theta_0} \quad (2.8) \]

\[ t_{1p} = \frac{2n_0 \cos \Theta_0}{n_0 \cos \Theta_0 + n_1 \cos \Theta_0} \quad (2.9) \]

\[ r_{1s} = \frac{n_0 \cos \Theta_0 - n_1 \cos \Theta_1}{n_0 \cos \Theta_0 + n_1 \cos \Theta_1} \quad (2.10) \]

\[ t_{1s} = \frac{2n_0 \cos \Theta_0}{n_0 \cos \Theta_0 + n_1 \cos \Theta_1}. \quad (2.11) \]

Through the use of Poynting's theorem, the reflection amplitudes can be used to calculate the intensity of the electric field such that:

\[ R_p = r_{1p}^2 \]
\[ R_s = r_{1s}^2 \quad (2.12) \]
\[ T_p = \frac{n_1}{n_0} t_{1p}^2 \]
\[ T_s = \frac{n_1}{n_0} t_{1s}^2. \]

### 2.3.2 Reflections at air/metal interfaces

Calculation of the electric vectors and field strengths for reflections from absorbing surfaces is more complicated, and computations using the equations based on theory often require iterative techniques. Estimates of the optical constants of the reflecting surface are made, often by transmission studies, and used in the equations and compared with the measured intensity and phase of the reflected light. New estimates are made and the iteration continues. Several simplifications of the complex equations can, however, be made. The following
equations are applicable for reflections from metal surfaces in which
\[ n^2 + k^2 \gg 1 \text{ [7]:} \]

\[
Rp = \frac{(n^2 + k^2) \cos^2 \Theta_0 - 2n \cos \Theta_0 + 1}{(n^2 + k^2) \cos^2 \Theta_0 + 2n \cos \Theta_0 + 1} \tag{2.13}
\]

\[
Rs = \frac{(n^2 + k^2) - 2n \cos \Theta_0 + \cos^2 \Theta_0}{(n^2 + k^2) + 2n \cos \Theta_0 + \cos^2 \Theta_0} \tag{2.14}
\]

2.3.3 Optics of multilayer films

Systems of layers of absorbing and nonabsorbing films are even more complex yet and must be treated with matrix formulas in which the characteristics of each film are taken into account. The required information includes the refractive indices (complex for absorbing films) and the thicknesses of all the films (see for example [190]).

Spectroscopic evaluation of thin films at grazing incidence is complicated by the optical effects inherent to thin films. Band shapes can be distorted by the changes in the refractive indices of the film materials through the frequency range of an absorption band. This process, known as anomalous dispersion, has been described by several authors [161, 168, 191]. Infrared absorption bands can be described by an increase in the extinction coefficient \((k)\) at a specific frequency. A more exact description of the reflection process involves the satisfaction of Maxwell's equations and boundary conditions at the film interfaces. This requires that both \(n\) and \(k\) vary through the absorption band as shown in Figure 2.9 [168]. For large absorptions, the change in \(k\) masks the small change in \(n\), and no evidence of the phenomena appears in the spectra. For small absorption bands at grazing incidence, the change in \(n\) distorts the shape of the absorption, shifting the absorption maximum to higher wavenumber and producing the derivative shape. Numerical calculations of the shape of absorption bands for various angles
Figure 2.9: Variation of the complex refractive index through the 1732 cm\(^{-1}\) absorption band of PMMA

of incidence, polarization states of the infrared beam, and substrate material have been published \[161,168\].

In order to characterize a thin film by reflection of light from the surface, several characteristics of the reflecting surface must be examined: 1) the nature of the incident light and its effect on the absorbing layer, 2) the resulting electric field at the surface of the structure, 3) the ability of the adsorbed layer to absorb the standing electric field, and 4) the nature of the reflected light beam. The most important consideration is that there must be an electric field present in the
vicinity of the layer to be examined. The characteristics of the incident light have much to do with the resulting electric field. The largest field is present at the surface for p-polarized light incident at a near grazing angle. On metal surfaces with large electron mobilities, the resulting electric field at the surface is highly oriented normal to the surface and enhanced relative to the incident beam by a factor of up to four. Cancellation of the horizontal field at the surface takes place due to the ability of the mobile electrons in a metal to mirror the electric field produced by the electromagnetic wave above the surface. As a result of this mirroring, the electric field in the horizontal direction relative to the surface is nulled. The selection rules described earlier hold rigidly for these surfaces with molecular vibrations normal to the surface interacting with the electric field. On surfaces other than metals, the resulting electric field is less specific, having components at the surface in each of the orthogonal directions. Semiconductor substrates, for example, lack the free electrons of the metal surface and cannot cancel the horizontal electric field. Spectral interpretation is more difficult due to the incomplete cancellation of the Ip electric field at the surface (see Bradshaw [192]).

There is much interest in obtaining the orientation and reaction information available for metal surfaces on semiconductor and other types of nonconducting surfaces. Very little work has been attempted on such surfaces. In an attempt to obtain information on the adsorption processes on silicon surfaces, Borg et al. [193,194] have published numerical simulations of the absorption of a theoretical monolayer on a superlattice of a metallic and semiconductor compound. The simulations were based on the reflection and transmission properties of thin films using the values of the optical properties of palladium and silicon. The optical properties of the adsorbate were also taken into account using
carbon monoxide as a model adsorbate. Theoretical calculations of the change in reflectivity at 2000 cm\(^{-1}\) for CO adsorbed on several Si/Pd surfaces are shown in Figure 2.10 (from Borg et al. [193]). The magnitude of the absorption depended on the reflection properties of the substrate and the polarization and angle of incidence of the incident light. As seen in Figure 2.10a, the absorption factor for the adsorbate on a silicon surface for an 84 degree angle of incidence was negative and less than one unit. The other extreme was the adsorbate on a metal surface alone as shown in Figure 2.10b. The absorption coefficient was large and positive. The other figures indicated the absorption coefficient for the cases of adsorption on a single semiconductor layer on the metal surface (2.10c) and absorption on the superlattice (2.10d). Note that the addition of the metal in the film structure increased the value of the absorption coefficient by several orders of magnitude.

It has been the goal of this work to verify and extend the use of infrared reflection-absorption spectroscopy to systems of thin films of semiconductor and catalyst materials. The principles described in the previous sections have been used to formulate, fabricate, and analyze several thin film structures of microelectronic and catalytic importance. The use of thin film structures for this purpose has been justified and the experimental results for those studies will be summarized next.
Figure 2.10: Calculated values of the absorption coefficient of CO on several Pd/Si substrates
3 PM-FTIRRAS SPECTROMETER DESIGN

3.1 FTIR Spectrometer

A major portion of this research has been the design of modifications to the standard FTIR spectrometer in order to make it "surface sensitive". In order to provide a full understanding of the optical and electronic processing involved in the technique and apparatus used in this work, a full description of the standard spectrometer will be given first. The sections that follow will then give the details of the modifications that were performed, the reasoning behind them, and spectral evidence of the improvements to the system.

3.1.1 Standard features

A Nicolet 60SX FTIR spectrometer has been modified to accommodate the polarization equipment. The 60SX FTIR spectrometer is a rapid scanning spectrometer consisting of a Michelson interferometer with a germanium-coated potassium bromide beamsplitter. The velocity of the moving mirror is manually set between values of 0.052 and 25.19 cm/sec allowing up to 60 scans per second to be collected. A mirror travel of 3 cm allows resolutions down to 0.10 cm$^{-1}$. The optics bench is purged with air that has been filtered to remove water and carbon dioxide. A dedicated Nicolet computer controls the optics bench and data collection, manipulation, and storage on a 20 megabyte hard disk storage module.
A diagram of the optical path of the spectrometer is shown in Figure 3.1 with a table of the descriptions of the components in Table 3.1. The infrared radiation emitted by a water-cooled glowbar source was directed through a variable aperture and then into the interferometer. The relative motion of a fixed mirror and an oscillating moving mirror produced a signal that varied with intensity and time known as an interferogram (for more information on FTIR theory, see Griffiths [18]). From the interferometer, the infrared beam passed to a movable mirror (MF4 in Figure 3.1) that directed the beam either to the microbeam compartment or to the standard sample chamber of the spectrometer. The beam was focused in the sample compartment by a parabolic mirror (M6) to a diameter of approximately 1/4 inch. The beam then traveled out of the sample compartment and was recollimated and sent to either of two detector ports on the optics bench. The beam was focused on the detector element by parabolic mirrors (M9 and M10). The velocity of the moving mirror was monitored and controlled by passing a HeNe laser (L1) beam through the interferometer with the infrared beam. This monochromatic beam produced a sine wave interferogram which was detected separately from the IR signal and used to calibrate the motion of the moving mirror in the interferometer. This ensured a constant mirror velocity necessary to obtain accurate peak calibration in the final spectra.

The infrared detector element produced a voltage that was proportional to the intensity of the infrared radiation impinging onto the element. As a result of the interferometer, the intensity varied with time (or mirror position). The signal was first sent through several gain stages controllable from the computer terminal. These were used in cases where the intensity at the detector was very weak, as in a strongly absorbing sample. The signal was then split into a differential signal (having (+) and (-) components that vary relative to each other) and sent to the
Figure 3.1: Diagram of the optical layout of a Nicolet 60SX Fourier transform infrared spectrometer
Table 3.1: Symbols used in schematic of FTIR optical components

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>standard glowbar source</td>
</tr>
<tr>
<td>S2</td>
<td>standard tungsten-halogen source</td>
</tr>
<tr>
<td>S3</td>
<td>optional source</td>
</tr>
<tr>
<td>MF1</td>
<td>computer controlled source selection mirror, 208 mm EFL</td>
</tr>
<tr>
<td>A1</td>
<td>computer controlled aperture</td>
</tr>
<tr>
<td>M2</td>
<td>flat mirror</td>
</tr>
<tr>
<td>M3</td>
<td>collimating off-axis parabolic mirror, 208 mm EFL</td>
</tr>
<tr>
<td>MF2</td>
<td>moving flat mirror to external source</td>
</tr>
<tr>
<td>BSIR</td>
<td>infrared/laser beamsplitter</td>
</tr>
<tr>
<td>M4</td>
<td>interferometer moving mirror</td>
</tr>
<tr>
<td>M5</td>
<td>interferometer fixed mirror</td>
</tr>
<tr>
<td>L1</td>
<td>reference laser</td>
</tr>
<tr>
<td>MF4</td>
<td>moving flat mirror to microbeam compartment</td>
</tr>
<tr>
<td>M6</td>
<td>sample focusing mirror, off-axis parabola, 237 mm EFL</td>
</tr>
<tr>
<td>M7</td>
<td>sample collection mirror</td>
</tr>
<tr>
<td>M8</td>
<td>flat mirror</td>
</tr>
<tr>
<td>MF5</td>
<td>2-position computer controlled detector</td>
</tr>
<tr>
<td>M9,M10</td>
<td>detector condensing mirrors, off-axis parabola, 64 mm EFL</td>
</tr>
<tr>
<td>M11</td>
<td>pre-aligned detector positions</td>
</tr>
<tr>
<td>M12</td>
<td>flat mirror</td>
</tr>
<tr>
<td>M13</td>
<td>microbeam condensing mirror, off-axis parabola</td>
</tr>
<tr>
<td>M14</td>
<td>64 mm EFL</td>
</tr>
<tr>
<td>M15</td>
<td>Z-axis microbeam computer controlled focussing mirror</td>
</tr>
<tr>
<td>M16</td>
<td>off-axis parabola, 64 mm EFL</td>
</tr>
<tr>
<td>M17</td>
<td>X-axis microbeam computer controlled mirror</td>
</tr>
<tr>
<td>M18</td>
<td>detector condensing mirror, off-axis parabola, 64 mm EFL</td>
</tr>
</tbody>
</table>
spectrometer computer for further processing. The process of splitting the signal was included in order to reduce the interference from nearby voltage sources along the relatively long path between the detector and the signal processing circuit board in the spectrometer. The signal was then recombined into a single-ended signal (having one voltage that varies with respect to ground) and sent through high- and low-pass variable-frequency electronic filters. These filters were controllable from the keyboard and were used to filter out frequencies that were outside the Fourier frequencies (for example, the 60 Hz signal due to the standard electrical power that operates much of the optics bench). They also eliminated "folding back" of absorption frequencies that are outside the infrared range of interest [18]. The Fourier frequencies were dependent on the velocity of the moving mirror in the interferometer, necessitating filters that could be adjusted for a variety of cutoff frequencies (see Table 3.2). The signal then passed into a 12 bit analog-to-digital converter (ADC) and then to a sample-and-hold circuit. The rate at which the ADC sampled the voltage signal was controlled by the timing laser described earlier. Each sample that the ADC collected corresponded to one data point in the interferogram that was stored in the computer memory. Many scans could be coadded and averaged in order to obtain a more accurate representation of the actual interferogram at the detector. The timing laser was once again used to signal the start of each scan in order to insure accurate coadding. The result was a more accurate Fourier transform of the data and an increase in the signal-to-noise ratio of the final spectrum.
Table 3.2: Table of values for the cutoff frequencies of the standard filters in the signal path of the 60SX FTIR

<table>
<thead>
<tr>
<th>setting</th>
<th>LPS</th>
<th>HPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>bypass</td>
<td>bypass</td>
</tr>
<tr>
<td>1</td>
<td>0.708</td>
<td>0.039</td>
</tr>
<tr>
<td>3</td>
<td>2.124</td>
<td>0.117</td>
</tr>
<tr>
<td>5</td>
<td>3.540</td>
<td>0.195</td>
</tr>
<tr>
<td>7</td>
<td>4.956</td>
<td>0.273</td>
</tr>
<tr>
<td>9</td>
<td>6.372</td>
<td>0.351</td>
</tr>
<tr>
<td>11</td>
<td>7.788</td>
<td>0.429</td>
</tr>
<tr>
<td>13</td>
<td>9.204</td>
<td>0.507</td>
</tr>
<tr>
<td>15</td>
<td>10.62</td>
<td>0.585</td>
</tr>
<tr>
<td>17</td>
<td>7.96</td>
<td>0.708</td>
</tr>
<tr>
<td>19</td>
<td>23.88</td>
<td>2.124</td>
</tr>
<tr>
<td>21</td>
<td>39.80</td>
<td>3.540</td>
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<tr>
<td>23</td>
<td>55.72</td>
<td>4.956</td>
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<tr>
<td>25</td>
<td>71.64</td>
<td>6.372</td>
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<tr>
<td>27</td>
<td>87.56</td>
<td>7.788</td>
</tr>
<tr>
<td>29</td>
<td>103.48</td>
<td>9.204</td>
</tr>
</tbody>
</table>
3.2 Modifications for PM-FTIRRAS

3.2.1 Optics

Few major changes were made to the standard optics bench of the 60SX FTIR in order to maintain the ability to use the spectrometer for other types of spectroscopy. Most additions to the optical system were mounted on an external optics bench adjacent to the FTIR. The standard sample compartment was used to accommodate the polarization-modulation optics. The infrared beam was polarized at a 45 degree angle with respect to the substrate by a silicon substrate Brewsters’ angle polarizer (Harrick Scientific, Inc. PTD-E1R). The plane of polarization was then modulated about the 45 degree angle by a zinc selenide photoelastic modulator (PEM) (Hinds International, series II). The modulator operated at a frequency of 37 kHz which corresponded to changing the plane of polarization from parallel to perpendicular to the plane of incidence at 74 kHz. The infrared beam left the sample compartment and traveled along the normal beam path of the spectrometer with one exception. The final focusing mirror (M9 in Figure 3.1) was replaced by a 3” x 3” flat mirror so that a collimated beam left the optics bench.

The PM-FTIRRAS cell, optics, and infrared detector were mounted on an auxiliary optics table constructed of 1/2 inch aluminum sheet (see Figure 3.2). Rubber pads were placed under the legs of the table in order to reduce building vibrations. The entire auxiliary optics bench was enclosed in a 1/8 inch Plexiglass cover to reduce dust contamination. The infrared beam itself was enclosed in a Plexiglass tube that was purged with the same air that purged the spectrometer bench. This reduced the absorptions due to atmospheric water vapor and carbon dioxide. Spherical focusing mirrors (Harrick Scientific, R= 305 mm) that focused
Figure 3.2: Optical layout for the PM-FTIRRAS experiments
the beam on the sample were mounted on aluminum mirror stands designed for this research which allowed alignment by 3 ultra-fine adjustment screws (Newport Research Corp.). The mirror mounts, cell, and the infrared detector were mounted on variable-height mounts and translation stages (Newport Research Corp.) which allowed alignment of the infrared beam to be made along the entire beam path. The beam was focused at grazing incidence on the sample, recollimated, and sent to a liquid-nitrogen cooled mercury-cadmium-telluride (MCT) detector.

3.2.2 Signal handling electronics

Additional electronics were required in order to demodulate the signal and extract the sample information. A schematic of the demodulation circuit is shown in Figure 3.3. A break was added to the signal path of the spectrometer immediately after the detector in order to direct the signal either along the standard route for transmission studies or to the demodulation loop for reflection studies.

As described in the literature review of the development of the technique [16], the highest sensitivity was realized by the technique when the final spectrum consisted of the ratio of the intensity difference \((I_p - I_s)\), to the intensity sum \((I_p + I_s)\). Further, an enhancement in the ability to ratio out the gas phase absorptions was possible by the simultaneous collection of the numerator and denominator signals. In order to achieve these goals, the demodulation loop consisted of three major features: 1) a split in the detector signal in order to produce two signals proportional to \((I_p - I_s)\) and \((I_p + I_s)\), 2) processing of the numerator signal by a lock-in amplifier and the denominator signal by a low pass filter, and 3) a switch circuit that allowed collection of both the numerator and denominator signals simultaneously.
Figure 3.3: PM-FTIRRAS signal demodulation circuit
Several additions were made to the circuitry used in this work in order to enhance further the signal quality of the final spectra. In the demodulation loop, the differential signal from the detector was first combined into a single-ended signal by a differential input amplifier. This allowed the entire signal at the detector to be used in the demodulation circuitry (which was limited to single-ended signals). The signal was then split into two paths, referred to as the numerator and denominator. The numerator signal was sent first to a band-pass filter (PAR 5011F) which was centered at the modulation frequency of the PEM. The detector signal consisted of the standard interferogram at the Fourier frequencies along with another interferogram, several orders of magnitude smaller, centered at the modulation frequency (see Figure 3.4). The band-pass filter effectively filtered out the large interferogram at the low frequencies in order to keep it from saturating the dynamic range of the lock-in amplifier. The signal was then sent to the lock-in amplifier (PAR 5207) which used as its reference a signal originating in the PEM. The lock-in output was proportional to the intensity difference (Ip - Is) [24] and appeared as a small interferogram on top of a DC signal. The output from the lock-in was then sent through a high-pass filter having a cut-off frequency of 100 Hz to filter out the DC offset. This signal was then sent to a switch circuit and combined with the denominator.

The denominator signal was first sent through a variable gain amplifier (1 to 100 times). This amplifier was added in order to be able to control the over all magnitude of the ratio (Ip - Is)/(Ip + Is). Since the sensitivity of the lock-in amplifier controlled the magnitude of the numerator interferogram, it was possible to magnify the numerator depending on the full-scale sensitivity setting. However, the 60SX would not allow transmittance values in the final ratioed spectrum that were greater than 200%. This variable amplifier allowed the denominator to be
Figure 3.4: Detector signal as a function of frequency during modulated experiments
magnified enough to keep the final spectrum below 200%. The denominator signal was then sent through high- and low-pass filters with a combined frequency "window" that encompassed the Fourier frequencies in order to eliminate folding back. This filtered signal was then sent to the switch circuit.

The switch circuit allowed the numerator and the denominator signals to be collected and stored simultaneously [23]. The switch used as references the signals generated by the spectrometer that controlled the data collection rate of the analog-to-digital converter (ADC). The switch alternately sent the numerator and denominator signals along the standard signal path to the ADC and to the computer for storage as an interferogram. Of the utmost importance in the use of the switch was the removal of other electronic components that would "mix" or "smear" the signals. One such component was the high- and low-pass filters in the standard signal path described earlier.

The process of switching between two different signals resulted in apparent high frequency components in the final interferogram. This concept is illustrated more clearly in Figure 3.5. Filters effectively "smear" high frequency components out of the signal by smoothing the data over several data points. This process of averaging would result in the undesirable mixing of the numerator and denominator signals. As a result, it was necessary to bypass the high and low pass filters in the standard signal path of the spectrometer while using the switched signal.

Another such component was the coadding of multiple scans to increase the signal-to-noise ratio. It was important to insure that each scan consisted of the even data points from the numerator and the odd points from the denominator but not a mix of the two. For this reason, a reset was placed on the switch in order to reset the switch position to the denominator path at the beginning of
Figure 3.5: Examples of interferograms from several optical systems: a) output of the lock-in amplifier, b) low pass filter output, c) combined interferogram from the switch circuit
each scan. The scan reference signal was generated by the timing laser and available at the front of the spectrometer. This insured that the first data point (and all the odd points) was always from the denominator (low-pass filter) and allowed the spectrometer to average multiple scans in order to increase the signal-to-noise ratio of the final spectrum.

Once stored in the computer as an interferogram file, software was written in the form of a Fortran program (Figure 3.6) to divide the combined interferogram into two interferograms: one with the even data points (numerator) and one with the odd points (denominator) from the original file. Subroutines IRTISK and IWTISK were received from Nicolet Instrument Corporation and used to extract and rewrite the data from the spectrometer data files. The new interferograms were then mathematically demodulated by Fourier transform and converted into intensity vs. wavelength curves known as single beam spectra.

The numerator spectrum (lock-in amplifier output) contained the information about the differences in the intensity between the two polarizations of light at the detector. This difference could be due to several factors as indicated in the following equation:

\[ \Delta I_{\text{total}} = \Delta I_{\text{sample}} + \Delta I_{\text{spectrometer}} \]  \hspace{1cm} (3.1)

An adsorbed molecule with a vibrational mode perpendicular to the surface is an example of an intensity difference due to the sample. Examples of differences due to the spectrometer may be a difference in the reflectivities of the polarizations at the substrate, the KBr windows of the cell, or the mirrors along the beam path. It is well established [6,7] that metal surfaces reflect the two orientations of polarized light differently, with the difference being greatest at grazing incidence (see Figure 2.3). For maximum sensitivity to the sample, the entire lock-in amplifier
INTEGER IHEAD(512),IDA(4100),DFN,FSZ5,IDAD(2050), IDAN(2050)

USE IRVAL TO LOAD FTIR PARAMETERS

IXSP=IRVAL(6165,1)
IXEP=IRVAL(6166,1)
DFN=IRVAL(6162,1)
FSZ5=IRVAL(6145,1)
INODE=IRVAL(13004,1)
NP=IXEP-IXSP
ITER=NP/4096

ZERO ALL ELEMENTS IN FOLLOWING TWO DESTINATION FILES

DO 10 I=1,1000
   IDA(I)=524288
10 CONTINUE

DO 20 I=1,FSZ5
   L=(1-I)
   CALL IWTISK(IDA,512,88+L*(DFN+1)*FSZ5,INODE)
   CALL IWTISK(IDA,512,88+L*(DFN+2)*FSZ5,INODE)
20 CONTINUE

READ FILE STATUS BLOCK AND COPY INTO FILES

CALL IRTISK(IHEAD,512,88+(DFN+1)*FSZ5,INODE)
IHEAD(23)=IHEAD(23)/2
IHEAD(17)=IHEAD(17)*2
CALL IRTISK(IHEAD,512,88+(DFN+2)*FSZ5,INODE)
CALL IRTISK(IHEAD,512,88+(DFN+3)*FSZ5,INODE)

READ SECTIONS OF DATA, SEPARATE, AND STORE IN SAME FILES

DO 40 K=1,ITER
   M=(K-1)*8
   N=M/2
   CALL IRTISK(IDA,4096,88+M*DFNZFSZ5,INODE)
   J=1
   DO 30 I=1,2548
      IDA(I)=IDA(J)
      IDAD(I)=IDA(J+1)
      J=J+2
30 CONTINUE
   CALL IWTISK(IDA,2548,88+(DFN+1)*FSZ5,INODE)
   CALL IWTISK(IDA,2548,88+(DFN+2)*FSZ5,INODE)
40 CONTINUE

CALL IREXIT
STOP
END

Figure 3.6: Fortran program used to split an interferogram data file into two files containing even and odd numbered data points
output would be due to absorptions of the sample. It has been suggested [16] that to compensate for dichroism of the optical path, a KBr plate could be added to the beam path between the sample and the detector. By varying the angle of the crystal with respect to the infrared beam, differences due to reflectivities of the spectrometer or cell could, in some cases, be minimized.

The increased sensitivity of the technique as a result of the addition of the KBr plate is shown in Figure 3.7. The figure shows the results for several optical systems for the analysis of a sample of CO adsorbed on a palladium film. Approximately 20 torr CO was present above the sample. The figure shows the spectra collected using successively more complex optical systems starting at the top. Spectrum a) was collected using a static polarizer in the sample compartment of the spectrometer. No modulation techniques were added to the system. The polarizer was manually rotated so that 2000 scans (1000 sec. collection time) were collected for Ip and Is. The resulting interferograms were Fourier processed and ratioed to give the spectrum. The only features in the spectrum were the periodic interference pattern caused by the silicon plates in the Brewster's angle polarizer and the fine structure near 2100 cm\(^{-1}\) indicative of incomplete cancellation of the gas-phase CO absorptions. Spectrum b) is a spectrum of the same sample taken with polarization modulation added to the optical system. No compensation was made for the \(\Delta I\) due to the optical system. Several other features appeared in the spectrum including larger bands in the 2100 and 2375 cm\(^{-1}\) regions, again indicative of incomplete cancellation of the gas phase CO and CO\(_2\), respectively. In addition, however, two other bands at 1957 and 2070 cm\(^{-1}\) were present. These bands were due to adsorbed CO on the surface and their positions compared favorably with the literature [77,79]. The band at 2070 cm\(^{-1}\) has been assigned to linearly bonded CO and the band at 1957 cm\(^{-1}\) to the CO adsorbed
Figure 3.7: IRRAS spectra of adsorbed CO on palladium using several different optical set-ups; a) static polarizer, b) modulation spectrum, c) modulation with KBr plate compensation
between two surface Pd atoms in a bridged configuration. The final spectrum c) shows the same sample with the addition of the KBr plate adjusted in order to compensate for the ΔI of the spectrometer. Because the sensitivity of the lock-in amplifier could be increased, the sensitivity to the adsorbed species was increased. The bands at 2070 and 1957 cm⁻¹ were clearly resolved and the miscancellation of the gas phase bands, evident in the other spectra, was corrected. This figure clearly shows the advantages of polarization modulation as well as the importance of compensating for the instrumental dichroism.

3.3 PM-FTIRRAS Cell

The cell to be used for the reflection studies is shown in Figure 3.8. Ports for KBr windows were mounted on opposite sides of a stainless steel reactor body just below the sample height to allow for a single reflection at grazing incidence from the sample surface. The sample, held against a copper holder by two small hold-down screws, was suspended from the sample holder and pointed “down” into the incoming reactant gases. The copper stand was heated by a heating element incorporated in the back of the stand. The element consisted of fine nichrome wire (0.4 mm) threaded through 1/8 inch, 4-hole ceramic tubing (Omega Engineering), and the assembly was cemented into the sample holder by high temperature cement (Fischer Scientific, Inc.). The element was connected to a variable voltage source through ceramic, high vacuum electrical feedthroughs (Insulator Seal, Inc.) and was capable of supplying up to 1000 watts of power to the sample holder. The cell bottom was removable and sealed to the cell body by a large-diameter Viton o-ring. The cell was capable of evacuation down to the 10⁻⁷ torr range.
Figure 3.8: PM-FTIRRAS cell used in the reflection studies
3.4 Gas Feed System

The feed system used to control and feed the reactant and adsorption gases is shown in Figure 3.9. The system was constructed primarily from 1/8 inch stainless steel tubing connected by either high pressure (Autoclave Engineering, Inc.) or Swagelok fittings. Carrier and feed gases were generally of 95% purity or higher. The gases were passed through several filters in order to remove residual oxygen and water vapor. After filtering, the gases were passed through thermal mass flow controllers (Brooks, Inc.) to monitor and control the flow rates. Several gas inlets were admitted into the cell in order to avoid contamination by flowing multiple gases through the same lines. Volatile samples were admitted to the cell by a six-port valve as shown in the figure. A 0.5 ml sample loop was placed in valve for gas phase samples. For continuous feeding of liquid or volatile solid samples, the small sample loop was replaced by a larger loop consisting of a section of 1/4 inch diameter glass tubing and Cajon ultra-torr fittings. For all samples, the valve and the gas lines downstream from the valve were heated to inhibit condensation before entering the cell. The sample stream entered the cell through the bottom directly at the sample. The products from the PM-FTIRRAS cell exited through the top of the cell and flowed through a stainless steel vacuum manifold or to vent. The vacuum system consisted of an oil diffusion pump (Edwards High Vacuum, Inc.) and a Sargent-Welch model 1402 roughing pump attached to a glass vacuum manifold. The system had a base pressure of approximately $5 \times 10^{-8}$ torr as measured by a thermocouple gauge and an ionization gauge tube. The glass vacuum manifold was connected to the PM-FTIRRAS cell through 1/4" stainless steel tubing with a six inch section of flexible tubing incorporated to allow for movement of the cell. The pressure in the
Figure 3.9: Diagram of the gas feed system used with the PM-FTIRRAS system
cell was monitored by a second thermocouple gauge mounted in the stainless steel vacuum manifold near the cell exit. This gauge allowed for vacuum monitoring in the cell during backfilling processes in which the glass vacuum manifold and the ionization gauge tube were isolated from the cell.
4 EXPERIMENTAL PROCEDURE

4.1 PM-FTIRRAS System Operation and Optimization

The operation of the PM-FTIRRAS system required the simultaneous operation of the FTIR spectrometer, the external electronics and added optical components, and the gas feed and sample treatment systems, depending on the type of experiment and the desired information. This section describes the additional procedures that were followed in order to facilitate the use of the polarization-modulation system over and above the normal procedures required in infrared spectroscopy.

4.1.1 FTIR operation and parameter settings

As mentioned previously, several modifications were required in the use of the FTIR in order to use the polarization-modulation system successfully. The first major modification was the optimization of the interferometer mirror velocity. The mirror velocity was limited by the time constant of the lock-in amplifier used to demodulate the detector signal. The time constant of a lock-in amplifier is a measure of the width of the frequency range or band around the reference frequency that is allowed to pass through the lock-in amplifier to the output. For the lock-in amplifier used in this study, the minimum time constant was 1 millisecond which translated to a frequency band of approximately 1000 Hz on
Table 4.1: 60SX FTIR parameter settings for PM-FTIRRAS spectrometer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>VEL</td>
<td>60</td>
<td>0.203 cm/sec</td>
</tr>
<tr>
<td>NDP</td>
<td>4096</td>
<td>4 cm⁻¹ res.</td>
</tr>
<tr>
<td>HPS</td>
<td>0</td>
<td>bypassed</td>
</tr>
<tr>
<td>LPS</td>
<td>0</td>
<td>bypassed</td>
</tr>
<tr>
<td>COR</td>
<td>HI, INT, or MD</td>
<td>high correlation</td>
</tr>
<tr>
<td>NSD</td>
<td>400</td>
<td>scans</td>
</tr>
<tr>
<td>APT</td>
<td>BL</td>
<td>fully open</td>
</tr>
</tbody>
</table>

Each of the high and low sides of the modulation frequency. In order for the interferogram to pass, the Fourier frequencies were required to be in the range of values below 1000 Hz. As seen in Equation 2.5, the mirror velocity must be kept near 0.200 cm/sec in order to allow the 400-4000 cm⁻¹ range to pass through the lock-in amplifier.

As mentioned earlier, the low- and high-pass filters of the standard signal path in the FTIR were bypassed (setting = 0) in order to inhibit smearing of the numerator and denominator signals before they were split into individual interferograms. In addition, the correlation between the last interferometer scan and the summed file was set at a high level. The 60SX FTIR had a method of comparing the newly collected scan with the summed file in order to sort out shifted or otherwise different scans that were due to vibration of the optics bench or changes in the sample. In PM-FTIRRAS, a shift of the interferogram by a single data point would result in mixing of the numerator and denominator signals. For this reason, the correlation value was set as high as possible (COR=HI, INT, or MD). A list of the parameter settings used for PM-FTIRRAS spectroscopy on the Nicolet 60SX is shown in Table 4.1. The aperture in the beam path was also opened fully in order to allow the maximum amount of infrared beam to reach the sample and detector.
4.1.2 Optimization of the PM-FTIRRAS system

The optical and electronic additions to the spectrometer system required some additional steps in order to obtain the maximum signal-to-noise ratio in the final spectra.

As with any optical spectroscopy, the alignment of the mirrors and samples in the optical path was crucial to the production of high quality spectra. In the present set-up, the sample actually acted as a mirror and was included in the optical alignment process. With the design of the PM-FTIRRAS cell shown in Figure 3.8, the sample holder was fixed relative to the rest of the optical system so that changing the sample did not require realignment. The focusing mirrors were mounted at a distance of 6 inches horizontally from the center of the sample and one inch below the sample height in order to optimize the sample size and beam usage as described in Equation 2.4. This setup gave an angle of incidence of approximately 82 degrees which matched the results of Equation 2.4 for a sample size of 2 inches and a beam diameter of 1/4 inch. The dispersion of the beam due to the focusing on the sample was fixed at 20 degrees total beam angle.

The phase adjustment of the lock-in amplifier relative to the detector signal was also crucial. In order to obtain the maximum signal at the output of the lock-in amplifier, the reference signal from the PEM was required to be in phase with the modulating detector signal (see Figure 4.1). The phase adjustment was performed manually using the controls on the lock-in amplifier. The output was monitored on both an analog scale and a digital readout while the phase was adjusted to null the output. As the output decreased, the sensitivity (full scale amplitude) of the lock-in was decreased in order to fine-tune the zeroing of the signal. A highly reflecting sample was present in the sample holder and the KBr
Figure 4.1: Illustration of the phase adjustment of the reference and sample signals with the resulting output of the lock-in amplifier.
compensation plate was normal to the infrared beam during the process. The amplitude of the PEM was set at the level to be used in the experiments. The phase was then changed by 90 degrees. The KBr compensation plate was then tilted in order to null the lock-in output again and the reference spectrum was collected. The phase adjustment was then set correctly and could be checked by changing the phase by 90 degrees and looking for a null in the output.

4.2 Thin Film Preparation

The samples used in the PM-FTIRRAS cell were prepared by evaporating thin layers of the reflecting materials onto commercially available silicon wafers or thin microscope cover glasses (Fischer Scientific Inc.). The silicon wafers used in this study were 2 inches in diameter and had electrical resistivities on the order of 1-10 μΩ-cm and thicknesses from 0.009-0.011 inches. The wafers were purchased from Aurel, Inc., and manufactured by Monsanto. Thin films of the reflecting materials were deposited by electron-beam evaporation in a bell jar system equipped with a Leybold-Hereaus TMP 450 turbo-molecular pump with a base pressure of approximately 1 x 10^-8 torr. The silicon samples were etched in a buffered HF solution to remove the native silicon oxide layer and washed in TCE, acetone, methanol, and distilled, deionized water. The cover glasses were scribed to fit into the 2 inch diameter sample holder and washed in methanol. Four wafers or six cover glasses were then mounted in the top of the bell jar vacuum system at a distance of approximately 20 cm from the tungsten source boats. The sources were small buttons of the various metals with purities generally above 99.5%. The system was pumped down to a vacuum in the 10^-7 torr range. The sources were melted with the electron-beam apparatus (Thermionics Laboratories, Inc.). A
shutter was then opened and the deposition took place on the wafers. Deposition thickness was monitored by a quartz-crystal oscillator (Kronos, Inc.) mounted at sample height and verified with an Alpha step profiler. The deposition rate was controlled by the amount of current through the electron beam and ranged between 50 and 200 angstroms per minute at chamber pressures between $5 \times 10^{-6}$ and $3 \times 10^{-5}$ torr. Films were deposited to a thickness of approximately 1200 angstroms unless otherwise indicated in the experimental description. During the evaporation, the sample temperature rose to 50-100 °C due to radiation from the source.
5 EXPERIMENTAL RESULTS

The underlying theme of this research project has been the extension of the application of infrared reflection-absorption spectroscopy to semiconducting and catalytic substrates through the use of samples prepared in the form of thin film structures. Thin film structures are characterized by the presence of an optically thin film of the material of interest deposited directly upon an optically thick, highly reflecting metal substrate or film. The basic assumptions in the use of thin film structures with PM-FTIRRAS are that: 1) the presence of a highly reflecting metal under a thin film of the material of interest would both enhance and orient the electric field in the vicinity of the adsorbate and 2) the surface properties of the sample would be characteristic of the semiconducting or catalytic material.

In order to demonstrate these processes, several different types of samples were analyzed. The quantitative aspects of the technique were characterized by the study of a commonly used thin film material (poly(methyl methacrylate)). The deposition of thin palladium films from palladium acetate was studied as a microelectronics application of the technique. The interaction between the acetate film and several different substrates was investigated. Finally, the analysis of thin films of molybdenum trioxide was used in order to show the value of the technique in the study of thin catalyst films.

The experimental results will be divided into five sections. Section 1 deals with the theoretical justification of the use of thin film structures in
PM-FTIRRAS. Section 2 covers the fabrication and characterization of the thin film structures. Section 3 considers the IRRAS results for PMMA films on the thin film structures in order to determine the sensitivity of the technique. The use of thin film structures for the study of palladium acetate interactions with semiconducting and metal films is treated in Section 4, and the analysis of molybdenum trioxide films in the study of catalyst thin film structures concludes in Section 5.

5.1 Theoretical Justification

The two most important characteristics in evaluating the sensitivity of PM-FTIRRAS for thin film structures are the magnitude of the electric field as a function of the distance along the surface normal and the relative reflectivities of the two orientations of the polarized light. These properties determine both the amount of interaction between the incident radiation and the sample and the ability to detect and measure the interaction. These quantities can be calculated theoretically using the principles of optics described in Section 2.3.

McIntyre [195] has reviewed the theory required for the mathematical evaluation of the reflection processes at thin film systems. The results of the calculations of the mean square electric field strength (relative to the incident field) as a function of the distance above the reflecting interface are shown in Figure 5.1. The results shown are for a highly reflecting surface (optical parameters $n_1 = 1.0$, $n_2 = 3.0$, $k_2 = 30.0$, $\Theta_1 = 45^\circ$) which is typical for most metals in the infrared region. While the values of the components of the electric field parallel to the interface are zero at the interface, the normal electric field due to the incident p-polarized light shows a maximum at the interface. The
Figure 5.1: Theoretical calculations for the mean square electric field strength as a function of polarization and distance above the interface
magnitude of the theoretical maximum depends on the angle of incidence by the value of \((4 \sin^2 \Theta_1)\). There are several processes by which a thin film may alter the magnitude of the standing electric field at a reflecting surface. The processes to be considered are: 1) the absorption of the field by the thin film, 2) the reflection of the incident beam by the air/film interface, and 3) the change in the angle of incidence at the film/metal interface due to the refraction of the incident beam. It is generally accepted that a very thin film \((d/\lambda < 10^{-3})\) does not significantly reduce the magnitude of the electric field at the film surface due to the small path length of the beam in the film. The processes of reflection and refraction may be calculated by the use of the equations in Section 2.3.

Calculations were performed in order to determine the magnitude of these phenomena for thin film structures consisting of a thin, nonabsorbing film on a metal substrate, and the results are shown in Tables 5.1-5.4. The variables in the tables refer to Figure 5.2. The calculations proceeded by, first, calculation of the initial reflection of the incident beam at the air/film interface \((I_p)\). Equation 2.8 was used for the calculation of the magnitudes of both the reflected beam and the transmitted, refracted beam. The angle of incidence was then calculated through the use of Snell's law for reflection at a nonabsorbing material. The reflection at the film/metal interface was then characterized by the use of Equation 2.13. The sum of the normal components of the incident and reflected beams was then used to calculate the magnitude of the standing electric field at the metal surface.

Table 5.1 shows the results for variation of the angle of incidence of the infrared beam on a silicon/copper thin film structure. The table shows some selected values for the angle of incidence at the metal surface \((\Theta_1)\), the magnitude of the reflected beam \((I_p)\), and the resulting electric field expressed in terms of the
Figure 5.2: Schematic diagram of the variables effecting the magnitude of the electric field at a reflecting surface
Table 5.1: Results of the reflection equations for thin film structures for variable angle of incidence

<table>
<thead>
<tr>
<th>$\Theta_0$</th>
<th>$\Theta_1$</th>
<th>$I_p$</th>
<th>E field</th>
</tr>
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<tbody>
<tr>
<td>degrees</td>
<td>degrees</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
<td>29.8</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>2.9</td>
<td>29.2</td>
<td>0.2</td>
</tr>
<tr>
<td>44</td>
<td>11.8</td>
<td>18.3</td>
<td>3.4</td>
</tr>
<tr>
<td>60</td>
<td>14.7</td>
<td>7.5</td>
<td>5.3</td>
</tr>
<tr>
<td>70</td>
<td>16.0</td>
<td>0.9</td>
<td>6.4</td>
</tr>
<tr>
<td>80</td>
<td>16.8</td>
<td>5.6</td>
<td>6.8</td>
</tr>
<tr>
<td>86</td>
<td>17.0</td>
<td>36.3</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Table 5.2: Results of the reflection equations for thin film structures for variable film refractive index

<table>
<thead>
<tr>
<th>$n_1$</th>
<th>$\Theta_1$</th>
<th>$I_p$</th>
<th>E field</th>
</tr>
</thead>
<tbody>
<tr>
<td>degrees</td>
<td>degrees</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1.0</td>
<td>82.0</td>
<td>0.0</td>
<td>366</td>
</tr>
<tr>
<td>1.4</td>
<td>45.0</td>
<td>32.2</td>
<td>137</td>
</tr>
<tr>
<td>2.0</td>
<td>29.6</td>
<td>26.5</td>
<td>43.7</td>
</tr>
<tr>
<td>2.5</td>
<td>23.3</td>
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<td>20.2</td>
</tr>
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<td>10.8</td>
</tr>
<tr>
<td>3.4</td>
<td>16.9</td>
<td>11.4</td>
<td>6.9</td>
</tr>
</tbody>
</table>

magnitude of the incident beam. The values of $I_p$ indicate a minimum corresponding to Brewster's angle for silicon near 72 degrees. The magnitude of the electric field was small, although the trend in the magnitude was a constant increase with increasing angle of incidence. These results suggest the maximum sensitivity would be obtained at the largest angle of incidence possible. As mentioned earlier, the largest experimentally obtainable angle was found to be near 82 degrees.

The results for fixed angle of incidence (82 degrees) and variable index of refraction of the film are shown in Table 5.2. The table shows that the refractive index of the film has a dramatic effect on the magnitude of the electric field. A
refractive index of 1.0 (simulating no film present) resulted in an enhancement of the field of approximately 3.7 times. The increase in the index resulted in a dramatic reduction in the enhancement. Near 1.4, the value for silicon dioxide, the enhancement was reduced to 1.37 times the incident value. The results suggest the use of thin film structures of oxides may provide more enhancement than materials with higher refractive indices.

Another consideration is the change in the relative reflectivities of the two orientations of polarization as a result of the thin film. The use of polarization modulation relies on nearly equal reflected intensities of the two orientations of polarization. Some compensation can be performed by the use of the angled KBr crystal in the optical path but only a small amount of compensation is available. McIntyre [195] has published the theoretical equations for the calculation of the change in reflected intensity of light as a result of the presence of a thin film. Although the equations for the ratio of the reflectivities of the two-phase system to the three-phase system are extremely complex, some simplification can be made by the expansion of the equations in $(d/\lambda)$. For very thin films $(d/\lambda < 10^{-3})$, terms in $(d/\lambda)^2$ and higher can be discarded. The resulting equations make up the linear expansion theory. The equations for both orientations of polarization are shown in Figure 5.3. Note that $\epsilon = (n^2 - k^2) - i(2\pi k)$ in the equations. The equations were used to calculate the percentage change (relative to the film-free substrate) in the reflectivities as a result of the film.

The results for several values of $\Theta_0$ are shown in Table 5.3. The other constants were those of silicon and copper as used previously. The values of $\Delta R_p$ and $\Delta R_s$ were strong functions of the angle of incidence with $\Delta R_p$ being the most strongly affected. $\Delta R_p$ rose continuously as the angle of incidence increased,
\[
\left( \frac{\Delta R}{R} \right)_\parallel = \frac{8\pi \, d \cos \phi}{\lambda} \Im \left( \frac{\hat{\varepsilon}_2 - \hat{\varepsilon}_3}{\varepsilon_1 - \hat{\varepsilon}_3} \right)
\]

\[
\left( \frac{\Delta R}{R} \right)_\perp = \frac{8\pi \, d \cos \phi}{\lambda} \Im \left\{ \left( \frac{\hat{\varepsilon}_2 - \hat{\varepsilon}_3}{\varepsilon_1 - \hat{\varepsilon}_3} \right) \left[ \frac{1 - (\varepsilon_1/\hat{\varepsilon}_2 \hat{\varepsilon}_3)(\hat{\varepsilon}_2 + \hat{\varepsilon}_3) \sin^2 \phi}{1 - (1/\hat{\varepsilon}_3)(\varepsilon_1 + \hat{\varepsilon}_3) \sin^2 \phi} \right] \right\}
\]

Figure 5.3: Linear approximation equations for the calculation of the effect of a thin film on reflectivities
Table 5.3: Results of the linear expansion theory for thin film structures for variable angle of incidence

<table>
<thead>
<tr>
<th>$\Theta_0$ (degrees)</th>
<th>$\Delta R_P / R$ (x 10^2)</th>
<th>$\Delta R_S / R$ (x 10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.7</td>
<td>30.0</td>
</tr>
<tr>
<td>50</td>
<td>1.0</td>
<td>25.4</td>
</tr>
<tr>
<td>60</td>
<td>1.8</td>
<td>19.8</td>
</tr>
<tr>
<td>70</td>
<td>5.0</td>
<td>13.5</td>
</tr>
<tr>
<td>80</td>
<td>44.5</td>
<td>6.8</td>
</tr>
<tr>
<td>82</td>
<td>95.3</td>
<td>5.5</td>
</tr>
<tr>
<td>88</td>
<td>500</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Table 5.4: Results of the linear expansion theory for thin film structures for variable film absorption coefficient

<table>
<thead>
<tr>
<th>$k_2$ (degrees)</th>
<th>$\Delta R_P / R$ (x 10^2)</th>
<th>$\Delta R_S / R$ (x 10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>9.5</td>
<td>5.5</td>
</tr>
<tr>
<td>0.03</td>
<td>10.1</td>
<td>5.1</td>
</tr>
<tr>
<td>0.10</td>
<td>11.5</td>
<td>4.2</td>
</tr>
<tr>
<td>0.15</td>
<td>12.6</td>
<td>3.5</td>
</tr>
<tr>
<td>0.20</td>
<td>13.5</td>
<td>2.8</td>
</tr>
<tr>
<td>0.24</td>
<td>14.3</td>
<td>2.3</td>
</tr>
</tbody>
</table>

indicating a desire to conduct the studies at less than grazing angles. The value of 9.5% at 82° was small enough to be compensated for by the KBr plate. The $\Delta R_S$ values shown in the table were all sufficiently small as well.

Table 5.4 shows the results for similar calculations for variable absorption coefficients of the film. An 82° angle of incidence was used in the calculations. The values were found to be relatively small, on the order of a few percent change in the reflectivities for both orientations of polarization.

The results shown in the tables support the requirements for the use of thin film structures for analysis of semiconductor and oxide surfaces. The calculations showed that the magnitude of the electric field at the surface of the film is
sufficient to interact effectively with adsorbed molecules while the reflection characteristics of the metal surface are maintained.

5.2 Analysis of Thin Film Structures

Thin film structures of silicon and copper were formed by electron-beam evaporation of the copper and silicon as described in Section 4.2. The copper was deposited first onto a cleaned microscope cover glass to a thickness of 1200 Å. The copper source was held in an alumina-covered molybdenum evaporation source boat (R. D. Mathis Co.) and was evaporated at approximately 100 Å/minute. Silicon was then evaporated onto the copper film, without breaking the system vacuum, by the use of the second evaporation source in the movable feedthrough of the source holder. The silicon was held in the source boat fitted with a carbon crucible liner (Thermionics Laboratories, Inc.). It was found that, without the crucible, the molten silicon wet the molybdenum or alumina boats and was not effectively evaporated. The oxygen content of the evaporated films was determined by Auger depth profiling and comparison of the relative peak heights of the signals. The vacuum ranged between $5 \times 10^{-8}$ torr during the initial pump down and approximately $5 \times 10^{-6}$ torr during evaporation of the copper and silicon. The thickness of the silicon layer was varied between 50 and 200 Å as measured by the quartz crystal oscillator.

The films were then analyzed to determine structure, morphology, and chemical composition. X-ray diffraction was used to determine the crystallinity and orientation of the evaporated films. Figure 5.4 shows the diffraction patterns for several samples. Pattern b) is the result for a single 1200 Å thick film of copper on a Pyrex cover glass. The peaks and relative intensities matched those
Figure 5.4: X-ray diffraction patterns of thin film structures of copper and silicon:
a) silicon/copper thin film structure, b) 1200 Å copper film
reported in the literature for the crystal planes of copper metal, indicating the films were crystalline with no orientation of the crystal planes relative to the surface. To the limit of sensitivity of XRD (approximately 2%), no evidence was found for the presence of bulk oxide phases in the copper. Pattern a) shows the results for a thin film (200 Å) of Si on a 1200 Å copper film. No diffraction lines for silicon were evident due to the sensitivity limit of the technique. The lines due to the underlying copper film were, however, broader and less intense due to the masking properties of the silicon layer.

The thin film structures were examined by scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) in a Perkin-Elmer model PHI 600 Scanning Auger Multiprobe system. The SEM results indicated the films were coherent, free of cracks, and smooth in appearance relative to the wavelength of light in the infrared region. Further analysis using AES combined with argon ion sputtering was used to determine the concentration of atoms as a function of depth. The resulting profiles showed the amount of interdiffusion and reaction between the films as a result of the deposition and further treatment of the substrate. Figures 5.5 and 5.6 show the results of the depth profiling of a 1200 Å copper film. The relative Auger signal height was scaled by the sensitivity factors of the respective atoms in order to determine the relative concentrations of the atoms. Oxygen was present on the surface due to the ambient oxide layer formed during exposure to air between the deposition process and the subsequent analysis. No oxygen was noted in the interior of the copper film to the limit of detection (approx. 0.1%). Near the substrate, the signal due to oxygen rose again due to the oxygen in the Pyrex. Evaporation of silicon over the copper resulted in the addition of the layer of silicon as shown in Figure 5.6. The depth profile indicated the concentration of oxygen in the silicon was constant throughout the
Figure 5.5: Auger depth profile of an evaporated copper film on a Pyrex cover glass
Figure 5.6: Auger depth profile of an evaporated thin film structure of silicon/copper
film at approximately 3%. The interface between the silicon and copper was somewhat broadened, indicating interdiffusion between the layers had taken place during the evaporation to form a solid solution. The Auger line shapes indicated that no reaction between the silicon and copper occurred. The oxygen concentration rose at the Si/Cu interface due to oxidation of the copper film in the $10^{-6}$ torr vacuum during the heating of the silicon source. The profile of the copper film under the silicon showed no indication of interdiffusion with the Pyrex substrate.

5.3 PM-FTIRRAS of Thin Film Structures

PM-FTIRRAS was then used to study the silicon/copper thin films. In order to calibrate the sensitivity of the thin film structures, thin films of PMMA of various thickness were spun on various substrates and analyzed using PM-FTIRRAS. PMMA has been used extensively in the study of thin optical films due to its well characterized refractive index and the ease of producing thin, uniform films by spin coating. It is important to remember that in the study of thin films by external reflection spectroscopy, the shape of the infrared bands and the appearance of the overall spectra differ, sometimes significantly, from the analogous transmission spectra.

As written by Greenler et al. [191] referring to the analysis of thin films:

"At second glance, it might appear that we are actually considering a usual transmission spectrum, with the radiation being transmitted through the sample layer, reflected at the metal surface, and transmitted again through the sample layer. When the sample layer is thin, compared to the wavelength of the incident radiation, this
concept is inappropriate. The amplitude of the electric standing wave field in the thin layer becomes the important factor and the path length of the ray becomes meaningless. One might say that the problem is one of physical optics and not of geometrical optics.”

The challenge has been to differentiate between the true chemical effects and the optical effects that may dominate in thin film systems.

5.3.1 PMMA/silicon/copper systems

The first part of these experimental results involved the comparison of infrared techniques in the analysis of thin films of PMMA on copper (1200 Å film on a cover glass), silicon (standard 2 inch silicon wafer), and silicon/copper thin film structures. Thin films of PMMA were prepared by spin-coating from solutions of PMMA in chloroform. The film thickness was varied by changing the concentration of the PMMA/CHCl₃ solutions. The spin rate was varied between 2000 and 4000 rpm. The film thickness was then measured using an ellipsometer (Gaertner Scientific Corporation, 6328 Å, 70° angle of incidence). The film thicknesses for the given concentrations are shown in Table 5.5. The film uniformity across the wafer was found to be approximately 10%.

The infrared spectra reported here show the wavenumber range between 2000 and 600 cm⁻¹. Although the range above 2000 cm⁻¹ showed the results for the C-H stretching region, the C=O vibrations were much more intense and more readily showed the relative sensitivity of each spectroscopic technique. The infrared spectrum of bulk PMMA is shown in Figure 5.7. The spectrum was collected by infrared transmission spectroscopy through a thick film of PMMA deposited by applying a PMMA/chloroform solution to a CsI infrared window and
Figure 5.7: Transmission infrared spectrum of PMMA
allowing the chloroform to evaporate. The absorption bands shown matched those of the published values [196]-[200] and were of the same relative intensities. The estimated film thickness for this sample was on the order of several microns.

Transmission spectroscopy was then used to obtain the spectrum of a thin film of PMMA on a standard silicon wafer. Figure 5.8 shows the spectrum for a film 800 Å thick. The silicon wafer was ratioed out of the spectrum so that only the absorption bands of the film appeared in the figure. Small infrared bands at 1726, 1436, and 1145 cm\(^{-1}\) were the only indication of the PMMA film on the surface. The PM-FTIRRAS system was then used to analyze the same film with the results shown in Figure 5.9. As described in the sections dealing with the reflection of light from semiconductor surfaces, no electric field enhancement took place at the silicon surface. The \(\Delta I\) (\(I_p - I_s\)) of the silicon surface alone, as indicated by the lock-in amplifier output, was large in comparison to the \(\Delta I\) of the thin PMMA film. As a result, the spectrum showed only a small indication of the PMMA film. In an effort to remove the effect of the silicon substrate, the PM-FTIRRAS spectrum of the silicon surface (spectrum c of Figure 5.9) was subtracted from the spectrum of the PMMA film. The subtraction result (spectrum a) showed no real increase in sensitivity to the PMMA film.

The sensitivity of PM-FTIRRAS to the surface of thin film structures relies
Figure 5.8: Transmission infrared spectrum of an 800 Å film of PMMA on a silicon wafer
Figure 5.9: PM-FTIR RAS spectra of an 800 Å film of PMMA on silicon: a) difference spectrum, b) PMMA on silicon, c) silicon wafer reference
on the presence of a reflecting metal surface both to enhance the electric field at
the surface and reflect both orientations of the polarization nearly equally.

Figure 5.10 shows the PM-FTIRRAS spectra of a 200 Å film of PMMA on copper.
A single small absorption in the spectrum of the copper substrate (b) at
945 cm$^{-1}$ was assigned to a thin film of Al$_2$O$_3$ on aluminum [201]-[203]. The
band was the result of the thin oxide layer on the aluminum mirrors along the
optical path of the spectrometer. The absorptions for the thin film of PMMA in
spectrum a) were clearly visible with the peak positions near the values for the
bulk spectrum. A slight upward shift in the peak positions of up to 5 cm$^{-1}$ has
been ascribed to optical dispersion effects [168]. One notable difference was the
absence of the strong absorption band near 750 cm$^{-1}$. This band has been
assigned to the COO deformation vibrational mode in the bulk sample, and its
absence in the reflection spectra indicated some degree of orientation of the
sample with respect to the surface. The orientation of the electric field normal to
the surface indicated that the $\delta$(COO) modes were parallel to the surface. Also
noted in the spectrum was the slight derivative shape in several of the small
absorption bands. This phenomenon has also been explained by optical dispersion
of the refractive indices of the films [168].

Similar results were obtained for a thicker film (800 Å) of PMMA on copper.
The results are shown in Figure 5.11. The absorption bands were near the
reported values, and all the bands were present except for the $\delta$(COO) vibration.
The full scale sensitivity of this spectrum was higher due to the increased
thickness of the PMMA film.

The results for the PM-FTIRRAS of the thin film structures of silicon and
copper are shown in Figures 5.12 and 5.13. The thin films were prepared as
described earlier with the PMMA solutions spun on the as-deposited substrates.
Figure 5.10: PM-FTIRRAS spectra of: a) a 200 Å film of PMMA on a copper substrate, b) copper substrate
Figure 5.11: PM-FTIRRAS spectra of: a) a 800 Å thick film of PMMA on a copper substrate, b) copper substrate.
Figure 5.12: PM-FTIRRAS spectra of: a) a 200 Å film of PMMA on a Si/Cu thin film structure, b) Si/Cu substrate
Figure 5.13: PM-FTIRAS spectra of: a) an 800 Å film of PMMA on a Si/Cu thin film structure, b) Si/Cu thin film structure
Estimates of the film thickness were made by analogy with the PMMA/copper films. Figure 5.12 shows the results for a 200 Å film of PMMA on a Si/Cu thin film structure. Spectrum b) in the figure shows the PM-FTIRRAS spectrum of the silicon layer on the copper film. A single broad absorption was present near 1100 cm$^{-1}$. The band was similar to the bands described in the literature for thin SiO films on aluminum mirrors [204] and was assigned to the Si-O bonds in the film. The band resulted from the small oxygen concentration in the silicon film. The bands for the PMMA in spectrum a) were close to the positions for the PMMA film on copper and of the same relative intensities, although the 750 cm$^{-1}$ band was absent. The band for the silicon substrate was still evident. Figure 5.13 shows similar results for a thicker film of PMMA on the same substrate. The relative size of the substrate Si-O band was decreased as the PMMA absorptions accounted for more of the $\Delta I$ of the system. The $\delta$(COO) band was evident at 751 cm$^{-1}$ although relatively weak in intensity.

In order to determine the lower limit of sensitivity of the technique, films of progressively smaller thickness were spun on a silicon/copper thin film structure. The results are shown in Figure 5.14. As evidenced by the spectra, PMMA films as thin as 20 angstroms were easily detected with the technique.

5.3.1.1 Discussion of results  The study of thin films and adsorbed molecules on semiconductor and insulating substrates by vibrational spectroscopy has been limited by the sensitivity of techniques. For infrared spectroscopy, the interaction of the incident light with the adsorbed molecule has in the past been masked by its undesirable interactions with the substrate. This interaction was clearly illustrated in Figure 5.9 in which an 800 Å thick film was barely visible on a silicon substrate. The approach taken in this work has been the fabrication of
Figure 5.14: PM-FTIRRAS spectra of PMMA films of various thickness on a Si/Cu thin film structure: a) 250, b) 80, c) 22 angstroms, d) Si/Cu substrate.
thin film structures of silicon and copper with the intent of changing the light interactions with the substrate to aid in the study of processes on the silicon surface.

The analysis of the PMMA films on the thin film structures was used as a method of analyzing the sensitivity of the structures to the presence of the thin films. The spectra in Figures 5.10-5.13 showed clearly that the use of thin film structures increased the sensitivity of the technique by increasing the strength of the electric field at the surface while reflecting both orientations of the polarized incident beam more equally.

In the case of PMMA films, very little interaction between the substrate and the film was evident from the infrared spectra. Previous work with thin polymer films has indicated that thin films act much like the bulk with little change in characteristics as the film thickness is decreased [176]. The absence of the \( \delta(\text{COO}) \) band in the spectra of the thin films suggests that the acetate groups were oriented normal to the surface in the first several layers with increasingly random orientation as the film thickness increased. Such information could add to the understanding of the processes of adhesion.

The sensitivity of the technique was shown to be sufficient to detect films approaching monolayer thickness. Although the band shapes in the spectra were altered due to the increasing contribution of optical effects, the analysis of very thin films was possible.
5.4 Palladium Thin Films

As an example of a microelectronics application of the use of thin film structures, the deposition of palladium thin films has been examined. Palladium has attracted much attention as metallization for contacts with both gallium arsenide and silicon substrates. Several investigations have been performed in order to understand better the metallurgical interactions between thin palladium films and gallium arsenide and silicon surfaces [205]-[208]. Refractory metal silicides have received much attention due to their electrical resistivities which are only slightly higher than their respective refractory metal films, and due to their resistance to oxidation at high temperatures (Murarka [209]). Palladium silicide has the advantage of a low formation temperature, approximately 250 °C, with some studies showing formation as low as 180 °C. Low temperature processes such as this are highly desirable in microelectronics fabrication because doping profiles carefully achieved in earlier fabrication steps are less apt to change. Palladium has the added advantage that it has a relatively low affinity for oxygen. Oxides of palladium require extreme conditions for formation. Contacts to silicon using palladium are stable and exhibit low electrical resistivities due to the formation of a metal-rich eutectic Pd$_2$Si.

5.4.1 Palladium thin film deposition processes

Thin films of most metals have been deposited using evaporation or sputtering processes. The relatively low melting point of palladium and its resistance to reaction with oxygen result in the production of high quality, high purity films. Evaporation or sputtering techniques are, however, limited by the relatively low throughput of the product and the need for patterning of the films.
after the deposition [210]. Other techniques exist for the deposition of thin metal films, including chemical vapor deposition (CVD) processes and depositions from thin film precursors. These techniques have the advantages of higher throughput, better step coverage, and less complex deposition apparatus. The search for volatile precursors for use in CVD processes has been quite extensive. In the last several years, the use of organometallic compounds for metal films has gained much of the attention. Film deposition by direct laser writing of the metal film pattern through either the precursor vapor or a thin, spin-coated film of the precursor has been used extensively. This process eliminates the need for further patterning of the metal film and reduces the number of processing steps involved in the fabrication process.

One such compound that has recently been investigated for the deposition of palladium films is palladium acetate (Pd(CH$_3$COO)$_2$). Preparation techniques have been reported in the literature with some associated characterization of the product. The molecule is prepared either by the addition of palladium nitrate to an acetic acid solution or by the dissolution of palladium sponge in hot glacial acetic acid with a slight addition of nitric acid [211]. The resulting precipitate was characterized to determine crystal structure and composition. It was determined that the molecule is represented by the formula:

$$\text{Pd(OOCCH}_3\text{)}_2$$ \hspace{1cm} (5.1)

with the palladium atoms in the $^+2$ oxidation state and bonded through the acid group in place of the acid hydrogen. However, under normal conditions (room temperature solutions) the molecule is present as a trimer [212] with the formula:

$$(\text{Pd}($\mu$ - OOCCH$_3$)$_2$)$_3$$ \hspace{1cm} (5.2)

with four acetate groups bridge-bonded between each palladium atom. The
bonding structure of the trimer is illustrated in Figure 5.15.

### 5.4.2 Palladium thin films from palladium acetate

Recently, several investigations of the use of palladium acetate for the deposition of thin palladium films have appeared in the literature [213]-[215]. The application of thin films of palladium acetate to the direct laser writing of metal lines has been investigated using Ar⁺ lasers. The decomposition process of the acetate molecule has a direct effect on the quality of the final films due to the incorporation of residual carbon and oxygen in the films, a common problem with the use of organometallic compounds. In one of the studies mentioned above [215],
the speed of the translation of the laser beam and the power of the continuous
wave laser were varied, and the resulting lines were analyzed by AES and SEM.
The process was a thermal decomposition of the palladium acetate as opposed to
the photochemical decomposition that is commonly used with organometallic
compounds. The decomposition temperature of the acetate film was determined
to be near 260 °C with the major reaction products being acetic acid and carbon
dioxide. The use of Ga⁺ beams ([214]) also resulted in metallic palladium films
for exposures of greater than 10¹⁴ ions/cm³. The films contained significant
amounts of organic material even at the highest exposures, with the lowest
contamination level being approximately 20% at the highest ion exposures.

The work outlined in this section considered the use of palladium acetate
(PdAc) as a precursor molecule for the deposition of palladium films. Little
previous work has focused on the decomposition mechanism or the effects of
substrate interactions on the deposition process.

Thin films of the acetate were prepared by solutions of chloroform of various
weight percent. Transmission infrared spectra of the acetate collected by several
different methods are shown in Figure 5.16. The thick film was prepared by
deposition of a chloroform solution on a CsI infrared window and evaporation of
the solvent. The KBr sample was prepared by standard infrared pellet pressing
techniques. The spectra were collected using 1 cm⁻¹ resolution and 1000 seconds
of scan time. The major band positions indicated the presence of the COO
asymmetric and symmetric vibrational modes of the acetate group at 1600 and
1400 cm⁻¹. A complete listing of the band assignments appears in Table 5.6. The
bands were assigned on the basis of published results for acetate and formate
ions [216]-[217]. Several bands have remained unassigned and were not assigned to
the PdAc molecule. The bands at 754 and 644 cm⁻¹, although present in the
Figure 5.16: Transmission infrared spectra of palladium acetate: a) thick film from a chloroform solution, b) KBr pellet sample
Table 5.6: Infrared band assignments for the palladium acetate

<table>
<thead>
<tr>
<th>Position (cm⁻¹)</th>
<th>Vibrational mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1606</td>
<td>(v_o (\text{COO}))</td>
</tr>
<tr>
<td>1420</td>
<td>(v_a (\text{CH}_3))</td>
</tr>
<tr>
<td>1400</td>
<td>(v_s (\text{COO}))</td>
</tr>
<tr>
<td>1372</td>
<td>(\delta (\text{CH}_3))</td>
</tr>
<tr>
<td>1328</td>
<td>(v_s (\text{COO}))</td>
</tr>
<tr>
<td>1021</td>
<td>((\text{CH}_3)\text{rock})</td>
</tr>
<tr>
<td>919</td>
<td>((\text{C} - \text{C}))</td>
</tr>
<tr>
<td>754</td>
<td>??</td>
</tr>
<tr>
<td>690</td>
<td>(\delta (\text{COO}))</td>
</tr>
</tbody>
</table>

thick film, were absent in the KBr pellet sample. The presence of decomposition products in the chloroform solution may account for the additional bands.

Thin films of the acetate were spun on several substrates in order to investigate the interaction with the substrate. Figure 5.17 shows the PM-FTIR spectrum of palladium acetate on a 1200 Å copper film. Large, well-defined bands were present at 1606, 1567, 1438, and 701 cm⁻¹. Other bands with derivative shapes were evident along the baseline. The differences between this spectrum and the spectra in Figure 5.16 were readily apparent. The large band at 1606 cm⁻¹ was split into two well resolved bands at 1606 and 1567 cm⁻¹. The bands at 1400 and 1372 cm⁻¹ in the bulk spectrum had shifted to 1438 and a small band at 1356 cm⁻¹. The 1328 band had disappeared completely. The bands in the lower wavenumber range were present as derivative shapes along the baseline.

Thin films of palladium acetate were also deposited on the thin film structures of silicon and copper. Figure 5.18 shows the results for a film deposited by spinning a 0.25% solution of palladium acetate in chloroform. The film thickness was estimated from comparison with the PMMA results to be near
Figure 5.17: PM-FTIR spectra of: a) palladium acetate film on copper, b) bare copper film
Figure 5.18: PM-FTIRRAS spectra of: a) palladium acetate on a silicon/copper thin film structure, b) thin film structure
250 Å. The reflection spectrum appeared much the same as the spectra for the film on the copper substrate. The only difference was the large broad absorption at 1074 cm\(^{-1}\) due to the silicon layer. The relative band intensities are similar to the PdAc films on copper with fewer derivative band shapes along the baseline.

Deposition of a thicker film (from a 1.0% solution of palladium acetate) resulted in the spectra shown in Figure 5.19. The infrared bands of the acetate were larger relative to the bands due to the silicon/copper substrate. In addition, the acetate bands in the 1100 cm\(^{-1}\) region appeared as small bands on top of the substrate absorption. The band intensities were of the same relative magnitude as the previous spectra.

Deposition of a thinner film (from a 0.1% solution) resulted in the spectra shown in Figure 5.20. The band due to the substrate layer was much more intense relative to the acetate bands. The film thickness was estimated to be less than 100 Å. The carbonyl vibrations were clearly visible although no other bands are discernible in the noise along the baseline. The relative band intensities were similar to those of the previous spectra.

5.4.3 IRRAS of palladium acetate decomposition

Palladium acetate has been shown by mass spectroscopy to decompose to palladium metal and acetic acid and carbon dioxide during high temperature processing using lasers and ion beams [213]-[214]. The literature value for the decomposition of the bulk acetate was found to be 260 °C. The mechanism of the decomposition has remained unclear after the previous studies. In this work, palladium acetate films were decomposed by heating the substrate under several ambient conditions. Figures 5.21 and 5.22 show the spectral results for the
Figure 5.19: PM-FTIR-RAS spectrum of: a) thick film of palladium acetate on a silicon/copper substrate, b) silicon/copper substrate
Figure 5.20: PM-FTIR spectra of: a) very thin film of palladium acetate on a silicon/copper substrate, b) silicon/copper substrate
Figure 5.21: Decomposition of PdAc/Cu in 10% O₂/He at 100 °C: a) initial spectrum, b) after 1 hour, c) 2 hours
Figure 5.22: Decomposition of PdAc/Cu in 10% O₂/He at 100 °C (cont.): a) 2.5 hours, b) 4 hours, c) 5 hours
constant heating of a thin film spun on a copper substrate under a 10% O₂/He atmosphere. The spectra were collected at 100 °C after several time intervals. Below 100 °C no changes in the spectra were noted, whereas at 100 °C the relative intensities of the bands changed dramatically, as did the baseline of the spectra.

The decomposition of a similar film in a 10% H₂/He atmosphere resulted in the spectra in Figure 5.23. The cell was evacuated to the 10⁻⁴ torr range before back-filling with helium and starting the hydrogen flow. The infrared bands of the acetate film decreased in intensity without heating the substrate. The relative intensities of the bands did not change nor did the baseline reflectivity of the system. Subsequent examination of the substrate indicated a film was present on the initial copper substrate, indicating the acetate did not simply evaporate or sublime from the surface.

Similar experiments were conducted on silicon/copper thin film structures in order to determine the effect of the substrate on the film decomposition process. The results for the decomposition in 10% O₂/He are shown in Figure 5.24. The spectra were collected at several temperatures as indicated in the figure. In contrast to the PdAc/Cu spectra, the decomposition did not take place until 145 °C, with little change in the absorption spectra as the decomposition proceeded. The relative intensities of the bands at 1603 and 1436 cm⁻¹ shifted slightly as the overall intensities decreased and the bands broadened.

The results for the decomposition in 10% H₂/He are shown in Figure 5.25. The results showed that the overall intensities of the infrared bands due to the acetate film decreased uniformly. However, for this case the film was stable in the hydrogen environment for over 12 hours. The appearance of a band at 1954 cm⁻¹ also differed from the results for the decomposition on the copper substrate.
Figure 5.23: Decomposition of PdAc/Cu in 10% H₂/He at room temperature: a) initial spectrum, b) after 30 minutes, c) 60 minutes
Figure 5.24: Decomposition of PdAc/Si/Cu in 10% O₂/He: a) initial spectrum at 100°C, b) 123°C, c) 145°C, d) 145°C for 20 minutes
Figure 5.25: Decomposition of PdAc/Si/Cu in 10% H₂/He: a) initial spectrum, b) after 12 hours at room temperature, c) at 75 °C
5.4.3.1 Discussion of results  The use of PM-FTIRRAS in the study of palladium acetate films was undertaken in order to understand better the processes taking place in the decomposition into palladium films. The spectra of the thin films of PdAc on the copper and silicon films indicated that structural and orientational effects were present in the films as a result of the film formation and subsequent reactions. The differences between the spectra of the bulk acetate and the films indicated a structural change in the molecule as a result of dissolution and spinning of the films. The infrared band positions of the acetate have been reported to be 1600 and 1427 cm$^{-1}$ [211] and 1602 and 1433 cm$^{-1}$ [213] for the asymmetric and symmetric COO vibrations. Comparison between the reflection spectra of the thin films of PdAc and the reported band positions of the bulk material resulted in the assignments of the bands at 1606, 1438, and 701 cm$^{-1}$ to the three vibrational modes of the COO group in the thin film samples. The band at 1567 was assigned to an uncoordinated COO$^-$ group as determined in reference [217]. Additional bands near the baseline were assigned to the CH$_3$ rocking mode (1020 cm$^{-1}$), the C-C stretching modes (919 cm$^{-1}$), and the CH$_3$ symmetric stretch modes (1372 cm$^{-1}$). The additional band at 1090 cm$^{-1}$, although not mentioned in the literature as a vibrational mode of the trimer, was assigned to combination bands of the acetate molecule. The possibility of formation of the monomer by the dissolution and spinning processes was ruled out by the necessity of heating the trimer in solution for monomer formation [211]. The presence of the 1328 cm$^{-1}$ band in the transmission spectra of both the thick film and the KBr sample indicated that it was associated with the acetate, and its absence in the reflection spectra suggested structural effects due to the spinning of the thin films. Considering the band assignments given earlier, the orientation of the C-CH$_3$ bond parallel to the surface may account for the absence of the band
in the reflection spectra. Several of the bands were assigned to impurities or degradation products in the source material. Upon spinning the chloroform of the solution on the substrates, the infrared spectra more closely matched the reported values, indicating that impurities may have been removed due to differences in the solubilities in chloroform.

The varying thickness of the films produced little change in the COO vibrational modes in the PM-FTIRRAS spectra. The strong C=O vibrations were evident in all the spectra, although the smaller bands were evident only in the spectra of the thicker films. No structural information as a result of the film thickness was evident. The relative intensities of the bands did not vary, indicating the molecules near the surface were not interacting strongly with the copper or silicon surfaces.

The decomposition of the acetate under several ambient conditions showed several new points. The spectra were used to monitor the structure of the acetate films as a function of the deposition conditions, with the onset of decomposition clearly notable in the resulting spectra. The previous studies of the acetate decomposition were conducted in air, and determined the decomposition temperature to be upwards of 200 °C. In these studies, it was clearly shown that the films decomposed under much milder conditions in the presence of hydrogen. Further, the spectra of the PdAc/Cu film in oxygen showed dramatic changes in the reflectivity of the substrate as the decomposition proceeded. The implication was that many impurities were incorporated in the film, lowering the reflectivity of the surface as a result of the carbonaceous deposits on the surface. The oxidation of the copper film could also not be ruled out, adding to the decrease in reflectivity of the surface. The presence of hydrogen in the atmosphere may result in the exchange of the hydrogen for the palladium atoms of the acetate, leaving
relatively volatile hydrocarbons as the decomposition products.

Comparing the results between the substrates also showed a trend in the decomposition conditions. The conditions leading to the decomposition were consistently more mild for the copper surface than for the silicon surface. These results suggest the possibility of the copper film catalyzing the decomposition of the acetate. The concept of metal atoms catalyzing the reaction has been mentioned previously in relation to the palladium atoms, although no mention of the effects of the substrate was made [213].

The results presented here show the usefulness of reflection-absorption spectroscopy in the analysis of thin film structures of semiconductor materials. The information obtained here would not be accessible by standard infrared techniques due to the nature of the semiconductor surface.

5.5 Thin Catalyst Films

Vibrational spectroscopy has been used extensively in the study of catalysts in order to characterize the molecules adsorbed on the catalyst surface during the reaction. Valuable insight has been gained by such studies as to the presence of intermediate species as a function of the reaction conditions. Unfortunately, many catalyst systems do not lend themselves to standard transmission IR studies. Oxide catalysts are often highly absorbing in the IR which inhibits the use of self-supporting wafers for analysis. The same limitation is noted for catalyst materials supported at high metal loadings on high surface-area supports. Other samples have low surface areas with the resulting number of adsorbed molecules being too low to detect. Such systems have remained largely uncharacterized because of these limitations.
PM-FTIRRAS of thin film structures offers an alternative method for the examination of these catalyst systems. Using the catalyst as the top layer of thin film structures avoids the limitations of low throughput and low surface area. The refractive indices of many metal oxides lie in the range of 1.4-2.5 which would result (as shown in Table 5.2) in an electric field at the surface adequate to allow detection of molecules on the catalyst surface. In addition, PM-FTIRRAS offers the capability over transmission spectroscopy for analyzing the catalyst surface with regard to the orientation of the molecules relative to the surface. Thin film structures of catalyst materials could, in many cases, be fabricated using modern thin-film deposition techniques. The resulting films could be oriented so that the top surface of the film comprised a single crystal plane, allowing information concerning the catalytic properties of individual crystal faces to be obtained.

5.5.1 Molybdenum trioxide thin films

In order to demonstrate the use of PM-FTIRRAS with catalyst thin film structures, thin films of molybdenum trioxide have been prepared and characterized with respect to their interactions with several C₄ hydrocarbons associated with the formation of maleic anhydride. Oxides of molybdenum have long been used in the oxidation of hydrocarbons. Earlier studies by this research group have shown molybdenum oxides to be active for the formation of maleic anhydride [218]-[220]. Molybdenum trioxide crystallites were found to be inactive for the oxidation of C₄ paraffins and olefins feeds but showed some selectivity to maleic anhydride when butadiene and furan were fed. The major products of the oxidation process were carbon oxides for all the hydrocarbon feeds.

Thin films of molybdenum trioxide were prepared by electron-beam evaporation. Pellets of molybdenum trioxide were pressed and then broken to fit
into an alumina-covered molybdenum evaporation boat. The pressure in the evaporation system rose to $2 \times 10^{-6}$ torr during the evaporation. The thickness of the films was monitored using the quartz crystal oscillator, using the specific gravity of molybdenum trioxide for conversion. Several metal films were used as the reflecting film under the oxide. Copper films were found to react under the oxidizing atmospheres of the reaction conditions with a resulting decrease in the reflectivity of the films. As a result, palladium films were substituted as the substrate reflector for the oxide films. The palladium films withstood the reacting conditions with little degradation or interaction with the oxide films.

The PM-FTIRRAS spectrum of the as-deposited films showed a single broad band that exhibits two maxima at 978 and 938 cm$^{-1}$ (see Figure 5.26c). The width of the band indicated that a variety of Mo-O bonds were present in the film. The other spectra in the figure show the results for the same film as the film was heated in an atmosphere of 10% oxygen/helium. The broad band split into two bands at 990 and 930 cm$^{-1}$ with a decrease in intensity. Further heating of the film to 300 °C resulted in a further splitting of the bands to 1000 and 956 cm$^{-1}$, with the appearance of a new band at 879 cm$^{-1}$. The width of the bands also decreased. The following figure shows the results of heating the film at 300 °C (Figure 5.27). As the duration of the oxidation increased, the band at 953 cm$^{-1}$ decreased in intensity as did the band at 879 cm$^{-1}$, with the final spectrum consisting of a single intense band at 1000 cm$^{-1}$ and several smaller bands at 945, 850, 824, and 670 cm$^{-1}$. The spectra show the structural and compositional changes in the oxide film as a function of the annealing conditions.

In order to demonstrate the use of thin film structures in the study of molecules adsorbed on catalyst films, several products and proposed intermediates
Figure 5.26: PM-FTIRRA spectra of a 200 Å molybdenum trioxide film on palladium: a) 300 °C in O₂/He, b) 200, c) as-deposited
Figure 5.27: PM-FTIRRAS spectra of an evaporated MoO$_3$ film at 300 °C in 10% O$_2$/He: a) 10 minutes, b) 30 minutes
in the formation of maleic anhydride from C4 hydrocarbons have been fed to the thin films of molybdenum trioxide. In this work 1,3-butadiene, γ-butyrolactone, and maleic anhydride have been passed over thin film structures of MoO3.

The results for exposure to 1,3-butadiene are shown in Figure 5.28. The thin film structure was evacuated to the $10^{-4}$ torr range in order to remove oxygen from the system. The cell was back-filled with helium, and the flow of helium was continued at approximately 200 cm$^3$/min throughout the experiment. 1,3-butadiene was pulsed over the films at several temperatures. No additional oxygen was admitted into the cell during the experiment. No change in the sharp band due to the molybdenum trioxide was observed until the temperature reached 350 °C, at which point the band due to the molybdenum trioxide disappeared completely. Similar results were observed for the other feed gases at elevated temperatures.

Upon the admission of oxygen into the cell after the exposure to 1,3-butadiene at high temperature, the molybdenum trioxide band reappeared as shown in Figure 5.29. Pulsing of the 1,3-butadiene over the thin film structure in the presence of oxygen resulted in a decrease in intensity of the band at 1000 cm$^{-1}$ and the disappearance of the band at 923 cm$^{-1}$ shown in Figure 5.30. A corresponding increase in the concentration of carbon dioxide in the vapor above the sample was evidenced by transmission IR.

The results for the adsorption of maleic anhydride on MoO3 are shown in Figure 5.31. The initial film was slightly reduced as evidenced by the large band at 958 cm$^{-1}$ (spectrum a). The substrate temperature and the temperature of the maleic anhydride saturator were 22 and 70 °C, respectively. The appearance of bands indicative of adsorbed maleic anhydride were evident in spectrum b).
Figure 5.28: PM-FTIRRAS spectra of molybdenum trioxide/palladium thin film structures in the presence of 1,3-butadiene vapor at the following temperatures (°C): a) 100, b) 200, c) 300, d) 350
Figure 5.29: PM-FTIRAS spectra during oxygen flow over hydrocarbon treated MoO$_3$ thin film structure: a) annealed film, b) initial film
Figure 5.30: PM-FTIRRAS spectra: a) during the combined flow of oxygen and butadiene over MoO₃/Pd at 300°C, b) initial film
Figure 5.31: PM-FTIRRAS spectra of: a) maleic anhydride on MoO₃/Pd thin film structure, b) initial substrate
The following figure (5.32) shows the results for purging the adsorbed maleic anhydride film with helium. The bands due to the film of maleic anhydride decreased in intensity and disappeared completely in the final spectrum.

A similar process and conditions were used to obtain spectra of γ-butyrolactone adsorbed on molybdenum trioxide thin film structures. Figure 5.33 shows the results for room temperature substrate and the saturator at 70 °C. The initial film was fully oxidized and oriented as evidenced by the single large band near 1000 cm\(^{-1}\). The exposure of the film to the butyrolactone vapor resulted in the appearance of bands at 1781, 1178, 1039, and 866 cm\(^{-1}\). After purging the cell with helium, the bands disappeared leaving the spectrum of the initial film.

5.5.1.1 Discussion of results The use of infrared reflection-absorption spectroscopy on thin film structures of metal oxide catalyst films has been demonstrated in the previous section. The spectra indicated that the technique was sensitive enough to analyze thin films of the catalyst material (<200 Å) when supported on a highly reflecting metal substrate. The spectra clearly showed the broad range of metal oxygen bonds present in the as-deposited film. The spectra also showed changes in both oxidation state of the films and orientation of the films as a result of further processing. The transmission infrared spectra of a series of molybdenum oxides has been reported previously [221]. The report indicates the presence of several absorption bands indicative of the MoO\(_6\) octahedra, the structure that dominates in the oxides and sub-oxides of molybdenum. The most predominant bands were those at 1000 and 875 cm\(^{-1}\) which were indicative of the presence of MoO\(_3\). The 1000 cm\(^{-1}\) band was assigned to the vibration of the terminal oxygen doubly bound to a single molybdenum atom. The 875 cm\(^{-1}\) band
Figure 5.32: PM-FTIRRAS spectra of maleic anhydride on a molybdenum trioxide/palladium thin film structure as a result of purging with helium: a) purging for 2 minutes, b) 20 minutes
Figure 5.33: PM-FTIRRAS spectra of: a) $\gamma$-butyrolactone on a MoO$_3$/Pd thin film structure, b) substrate
was assigned to the Mo-O-Mo vibration. Vibrational bands for the sub-oxides were found between these bands at 980, 950, and 892 cm$^{-1}$ and below 875 cm$^{-1}$.

Comparing these results with the results in Figure 5.26, the as-deposited films appeared to be slightly oxygen deficient. This was not unexpected due to the oxygen deficient atmosphere under which the films were evaporated. Upon annealing in oxygen, the bands at 1000 and 875 cm$^{-1}$ appeared along with the band at 956 cm$^{-1}$. The band at 956 cm$^{-1}$ was attributed to molybdenum in a lower oxidation state, as the band was present in the transmission spectra of the sub-oxides down to MoO$_2$. The gradual disappearance of this band was attributed to the oxidation of the film to molybdenum in the +6 oxidation state.

Other information could be gained from the spectra in the figures. The final spectrum showed a single band at 1000 cm$^{-1}$ with no other bands in the lower wavenumber region. Assuming the films were completely oxidized, the lack of other bands must be assigned to the orientation of the crystal planes of the film with respect to the surface. With the assignment of the 1000 cm$^{-1}$ band to the terminally bonded Mo=O, the spectra indicated that the film was oriented with the (010) crystal plane parallel to the surface and the Mo=O bonds oriented perpendicular to the surface.

The high temperature studies clearly showed the ability of PM-FTIRRAS of thin film structures for the investigation of orientational and compositional changes in thin catalyst films under reaction conditions. In the presence of 1,3-butadiene at high temperature (300 °C), the effect of the catalyst film was the complete combustion of the hydrocarbon with the corresponding reduction of the oxide film. The redox cycle was completed by the addition of oxygen to the system after the hydrocarbon treatment, with subsequent reappearance of the oxide band in the oriented configuration. The presence of both the hydrocarbon
and oxygen over the catalyst film resulted in the loss of the 923 cm$^{-1}$ band with little decrease in intensity of the band at 1000 cm$^{-1}$. This information may suggest different activities of the specific oxygen species toward the oxidation of the hydrocarbon, with the doubly bonded molybdenum atoms being less active. The concept of differing activities has been suggested previously [222].

The adsorption of the hydrocarbons showed the usefulness as well as the limitations of the use of PM-FTIRRAS for \textit{in situ} catalytic studies. In the fully saturated sample conditions (substrate colder than the source), bands due to a condensed phase of the feed material were evident on the sample surface. The thickness of the condensed phase was most likely several monolayers, at least, considering the the overall similarity between the bulk and condensed phase spectra. These bands were easily visible even though the gas phase above the sample was highly absorbing.

Figures 5.34 and 5.35 compare the spectra of butyrolactone and maleic anhydride in the bulk (a), vapor (b), and condensed (c) phases on the molybdenum trioxide thin film structure. In the case of maleic anhydride, the number of bands dropped significantly between the bulk and vapor spectra primarily because of the purification of the sample (the major impurity was maleic acid which has a much lower vapor pressure). The position and relative intensities of the bands of the condensed phase matched those of the vapor spectrum, suggesting little interaction with the surface. The same result was generally true for the butyrolactone, although a band at 1458 cm$^{-1}$ in the condensed phase spectrum did not appear in the vapor spectrum. Such differences may suggest the possible orientation of the molecules on the surface.

The lack of infrared bands in the spectra of the heated substrates suggested
Figure 5.34: Comparison of spectra for liquid (a), vapor (b), and condensed (c) butyrolactone on MoO₃ thin film structure
Figure 5.35: Comparison of spectra for solid (a), vapor (b), and condensed (c) maleic anhydride on MoO₃ thin film structure
several possibilities. Molybdenum trioxide has been shown to combust hydrocarbons readily to carbon oxides [220], with the resulting reduction of the oxide catalyst. For infrared bands to be present for molecules on the surface, the molecules must be adsorbed on the surface for a finite length of time. The possibility of immediate combustion of the hydrocarbon molecules on the surface could not be ruled out. The other possibility was the number of adsorption sites present on the effectively planar catalyst surface. The relatively low vacuum conditions used in these experiments, as well as the necessity of exposing the films to air between evaporation and the experimentation, could have left a large percentage of the available cites contaminated or filled with atmospheric impurities. The use of ultra-high vacuum techniques and in situ formation of the catalyst/metal thin film structures would provide the answers to these questions.

These results clearly indicate the usefulness of infrared reflection-absorption spectroscopy of thin film structures in the analysis of both reaction and orientational processes of catalyst thin films.
6 CONCLUSIONS AND RECOMMENDATIONS

The use of infrared reflection-absorption spectroscopy for the study of semiconductor and catalytic materials has been demonstrated through the use of thin film structures. High sensitivity to thin films of poly(methyl methacrylate) was exhibited for thicknesses down to the range of several monolayers as used in this study. Orientational effects were exhibited by the polymer films near the interface indicating limited interaction with the substrate as a result of the spin coating process.

The thin film structures were then used to characterize the interactions of palladium acetate with metal and semiconductor substrates. It was found that thin films exhibited structural changes as a result of spinning of the thin films. Subsequent processing using several ambient conditions showed dramatic variation in the resulting films with indications that the substrate affects the decomposition process.

In the analysis of catalyst thin film structures, the limitations of infrared transmittance and surface area were avoided. PM-FTIRRAS was used to analyze both the structure and composition of the catalyst and the adsorbed molecules on the catalyst surface. These studies were conducted in actual reacting conditions which illustrated the ability of the technique to discriminate against randomly oriented molecules in the gas phase above the sample surface.

The reaction of C₄ hydrocarbons over MoO₃ thin film structures indicated a
high degree of orientation of the film as well as a difference in the specific activities of several types of Mo-O bonds in the catalyst.

The results presented here suggest the enormous potential of the use of PM-FTIRRAS with thin film structures. In order to increase the amount of information obtainable, monolayer sensitivity on the catalyst surface must be achieved. The theoretical and experimental results presented indicate that the technique is sensitive enough to perform these studies. The addition of UHV conditions is, however, required to "activate" a higher percentage of the surface sites on the low-area surfaces. The incorporation of mass spectrometry would also add greatly to the information available by the correlation of the presence of adsorbed molecules with the product distribution. The high sensitivity of mass spectrometry would be necessary to evaluate the extremely low volume of molecules produced on the low-area surfaces.

Further investigations into the sample preparation techniques, including sputtering and plasma deposition processes, should be investigated in order to produce more highly ordered, uniform thin film structures of specific orientation. Such processes would yield valuable information concerning the catalytic activity of individual crystal faces.

Finally, the effect of the underlying reflecting surface cannot be overlooked. In these studies, the assumption of complete isolation of the metal film from the top surface of the thin film structure was assumed based on the Auger and SEM data. The porosity of the catalyst film would dictate the real activity of the metal surface, especially for such metals as palladium that exhibit strong catalytic activity (e.g. the dissociation of hydrogen).

The combination of UHV capability, with in situ formation of the thin film structures, and mass spectroscopy and infrared reflection-absorption spectroscopy
could add dramatically to the understanding of reaction processes on semiconductor and catalytic materials.
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Finally, I am proud of and thankful to my wife, Lisa, for her courage and fortitude through the last several years in preserving the home life even when research had to come first. Her sacrifices have not gone unnoticed.
9 APPENDIX: PM-FTIRRAS circuit diagram

Design requirements: S. Finke
Circuit design: H. Skank
Layout: J. Erickson

Ames Laboratory Instrumentation Shop
File #22307-001
Power requirements

Signal input and variable amplifier
Lock-in amplifier input and high and low pass filters
Timing signal inputs
Switch circuit and signal output