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The Growth, Structure, and Thermal Stability of Vapor Deposited
Ultra-thin Metal Films: Rh on Ag(100), Au on Pd(110), and Pt on
Pd(110)

by

Schmitz, Peter

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Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

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The growth, structure, and thermal stability of vapor
deposited ultra-thin metal films: Rh on Ag(100),
Au on Pd(110), and Pt on Pd(110)

Peter John Schmitz

Under the supervision of Patricia A. Thiel
From the Department of Chemistry
Iowa State University

The growth, structure, and thermal stability of ultra-thin metal films is investigated using surface sensitive techniques. The three systems studied present a variety of differing characteristics which can contribute to the growth mode, two-dimensional structure, and thermal stability of the films. The main factors contributing to the differing properties of the three systems presented here are: (1) the different substrate morphologies; (2) the differences in surface free energies between the overlayer and the substrate; (3) the degree of lattice mismatch for a particular system; and (4) the extent of miscibility of the two metals. These characteristics allow a means of comparison for the three systems studied.

The Rh films are found to grow in a pseudo layer-by-layer manner on Ag(100) at 300 K. At higher temperatures Ag migrates to the surface of the Rh films forming a Ag-Rh-Ag sandwich structure. The differences in surface free energies, the high mobility of the Ag atoms, and the

immiscibility of the two metals is thought to govern the equilibrium structure of this system.

The Au films on Pd(110) grow layer-by-layer for the first two layers, followed by a trend toward three-dimensional growth for thicker films. The Au films reconstruct to a (1x2) superstructure at two monolayers, and to a (1x3) structure at higher coverages. This transition between the (1x2) and (1x3) is postulated to originate from a break down in the two-dimensional order as three-dimensional growth begins, which favors the formation of the (1x3) structure.

The Pt films on Pd(110) follow a pseudo layer-by-layer growth at low temperatures, with three dimensional growth occurring at higher temperatures. The (1x2) and (1x3) superstructures are also observed for this system, the transition between the two being temperature dependent. Presumably the Pt is kinetically trapped into layer-by-layer growth at low temperatures. However, at higher temperatures three dimensional growth begins resulting in a similar transition between the two phases as is observed for Au on Pd(110).

Fundamental research on metal overlayers, such as that described here, provides meaningful information on phenomena which govern interface formation and film growth processes.

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Peter John Schmitz

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TABLE OF CONTENTS

	Page
DEDICATION	iii
GENERAL INTRODUCTION	1
PAPER I: NOVEL METAL FILM CONFIGURATION: Rh ON Ag(100)	6
PAPER II: Au FILMS ON Pd(110): Pd INDUCED CO DESORPTION FROM Au AND COVERAGE DEPENDENT (1x2) AND (1x3) Au RECONSTRUCTIONS	56
PAPER III: Pt FILMS ON Pd(110): DEPENDENCE OF (1x2) AND (1x3) RECONSTRUCTIONS ON FILM THICKNESS AND DEPOSITION TEMPERATURE	119
CONCLUSIONS	187
REFERENCES	191
APPENDIX A: Ir FILMS GROWN ON Pd(110)	194
APPENDIX B: ISOTOPE EFFECT IN WATER DESORPTION FROM Ru(001)	209
APPENDIX C: KINETIC ANALYSIS OF THE A ₂ THERMAL DESORPTION STATE OF D ₂ O ON Ru(001)	237
ACKNOWLEDGEMENTS	251

DEDICATION

In memory of my cousin,
Tom O'Conner.

GENERAL INTRODUCTION

Thin films offer the possibility of unusual properties which may be scientifically interesting and commercially useful. The growth of one metal atop another creates an interface through which new and interesting properties may be generated. If a film is thin enough, the film material may possess properties vastly different than its parent bulk material. This possibility has stimulated rapid growth in thin film research over the past decade. Considerable attention has been given to the electronic, chemical, and magnetic properties of thin films.

The deposition of a thin film results in the creation of an interface through which new electronic information can be transferred to the film material. The interaction of gas phase particles with a newly created film surface is one means of measuring the electronic perturbation of a metal film by its support medium. This has been shown by the work of Ruckman et al. (1), Ruckman and Strongin (2), and Pan et al. (3). When Pt and Pd monolayers are deposited on Ta(110) and Nb(110) they are found to be entirely passive to CO chemisorption at room temperature, a property quite different from surfaces of bulk Pt, Pd, Ta, and Nb (1-3). This has been associated with a modification of the density of states in the film resulting from an electronic alteration made through the interface (1-5). Analogous results have been reported for CO adsorption on Pt monolayers on W(110) (6), and for Pd monolayers on W(110) (7), Mo(110) (8), and Au (111) (9).

Research on the chemical properties of metal films has also been

motivated by the unusual properties of bimetallic, dispersed catalysts (10), and by the hope that thin films of metals on well characterized single crystal surfaces will serve as suitable models for understanding these properties. A thin film system which has been proven as a suitable model is that of Cu/Ru(001). For the catalytic dehydrogenation of cyclohexane to benzene, Peden and Goodman have shown that the rate of reaction can be enhanced by several orders of magnitude with this catalyst, relative to a copper-free ruthenium surface (11,12). The rates of reaction for this thin film system are identical under comparable conditions to that found for a dispersed, bimetallic Cu-Ru catalyst (11,12). Another example of the different chemical reactivity of thin films is provided by the work of Sachtler et al. (13-15), and Sachtler and Somorjai (16). They have found that a monolayer of Au on Pt accelerates the rate of cyclohexene dehydrogenation to benzene by a factor of five, relative to the bare Pt substrate, and that one to two layers of Pt on Au have about the same effect (13-15). A bulk Au surface is chemically inactive in cyclohexene dehydrogenation, so this again is a situation where creation of an interface results in strikingly different surface properties than could be obtained from either metal alone.

The magnetic properties of thin metal films such as Fe, Ni, and Co have received much attention. Surface layers of these ferromagnetic materials are generally believed to have reduced magnetic moments relative to the bulk. Significant disagreement, however, has developed over the way in which the properties of these films vary with thickness and temperature (17-24). The disagreement has been suggested to arise

from a variation of film configuration and film composition with temperature, properties which are poorly understood (17,21,25,26). These factors can significantly effect the magnetic properties of the films (17). The present controversy in magnetic films seems to be responsible for the recent surge of interest over the topic of metal film growth.

Recent research in thin films has been motivated by new electronic, chemical, and magnetic properties which evolve when metal layers are stabilized on various substrate materials. It has been the goal of thin film research that the study of metal films on well characterized single crystal substrates will serve as a suitable model for understanding these new properties. However, as has been shown for the area of magnetic films, the properties of a particular film substrate combination cannot be fully understood unless its structure and thermal stability is correctly ascertained. Similarly, the different catalytic properties of films may be due to the chemical properties of different film morphologies (i.e., smooth vs. flat monolayers), or to special reactive sites, such as misfit dislocations or cluster edges. Because surface structure is fundamental to surface properties, it is of interest to study the structural characteristics of ultra-thin metal films (1 to 10 monolayer regime). However, a fundamental understanding of the microscopic processes which lead to that structure needs to be developed.

It is the purpose of this dissertation to use surface science techniques to study the growth of ultra-thin metal films in order to better understand the interfacial phenomena which influence the development of the films structure and thermal stability. We primarily

utilize Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and thermal desorption spectroscopy (TDS) to study the growth, structure, and thermal stability of a series of metal film combinations. The three systems on which we concentrate our efforts are: Rh on Ag(100); Au on Pd(110); and Pt on Pd(110). These three systems present a variety of differing characteristics which can contribute to the growth mode, two-dimensional structure, and thermal stability of the films. The main factors contributing to the differing properties of the film-substrate combinations presented here are: (1) the different substrate morphologies, (100) vs. (110); (2) the differences in surface free energies between the overlayer and substrate; (3) the degree of lattice mismatch for a particular system; and (4) the extent of miscibility of the two metals. These characteristics allow us a means of comparison for the three systems studied.

The purpose of this work is not to discover new interesting electronic, or chemical properties for these systems, but rather to significantly vary the overlayer-substrate properties to try to gain some insight into how these properties can be related to the growth and resulting structure of the different systems. Fundamental research on metal overlayers, such as that described here, provides meaningful information on phenomena which govern interface formation and film growth processes. The hope one day is to be able to understand the basic phenomena which control film growth such that metal films can be tailor made to enhance a particular property which is of scientific or commercial importance.

Explanation of Dissertation Format

This dissertation is arranged according to the alternate style format. Three papers are included. Paper I, "Novel Metal-Film Configuration: Rh on Ag(100)", appears in Volume 40 of The Physical Review B on pages 11477-11487, 1989. Paper II, "Au Films on Pd(110): Pd Induced CO Desorption From Au and Coverage Dependent (1x2) and (1x3) Reconstructions", will be submitted to Surface Science. Paper III, "Pt Films on Pd(110): Dependence of (1x2) and (1x3) Reconstructions on Coverage and Deposition Temperature", will be submitted to The Physical Review B.

PAPER I:

NOVEL METAL-FILM CONFIGURATION:

Rh ON Ag(100)

NOVEL METAL-FILM CONFIGURATION:

Rh ON Ag(100)

P. J. Schmitz, W. -Y. Leung, G. W. Graham, and P. A. Thiel

Department of Chemistry and Ames Laboratory

Iowa State University

Ames, Iowa 50011

ABSTRACT

We present the results of an investigation of Rh films on Ag(100). The films are studied using AES, LEED, XPS, UPS, ISS, and SAM. Overlayer characteristics are examined at substrate temperatures of 300 and 600 K. We find that the equilibrium configuration is not predicted by any of the three traditional growth modes (Frank-van der Merwe, Stranski-Krastanov, or Volmer-Weber). Rather, the equilibrium film structure is that of a Ag-Rh-Ag sandwich, most probably flat. Formation of the sandwich is thermodynamically driven by the difference in surface free energies between Ag and Rh, and is kinetically accessible because of the high mobility of the Ag atoms.

I. INTRODUCTION

In recent years there has been a tremendous increase in the number of investigations of metal-on-metal systems. Interests have ranged from fundamental studies of epitaxy to catalytic studies of bimetallics (e.g., 1-3). In most studies the motivation has been to determine the influence of the substrate on the properties of the overlayer film. To fully understand these substrate-overlayer interactions one must first know the structure of the overlayer film. Therefore, many efforts have focussed on overlayer growth, and the way in which electronic properties depend on the structure of the overlayer.

Most metal-on-metal studies are approached with the expectation that the film will grow in one of the three classical modes (4): sequential filling of layers (Frank-van der Merwe); agglomeration into three dimensional crystallites (Volmer-Weber); or growth of one or more layers followed by agglomeration (Stranski-Krastanov). The equilibrium growth mode in these systems is thought to reflect a balance between three thermodynamic factors: the surface free energy of the film, γ_f ; the surface free energy of the substrate, γ_s , and the interfacial energy, γ_i . It is often beneficial to have ordered layer growth, e.g., layer growth is desired when studying the electronic states of metal overlayers because this makes it possible to model the substrate-overlayer system (5). For this reason, as well as for practical reasons of ease of preparation, substrate-overlayer combinations are often chosen such that $\gamma_f \leq \gamma_s$. However, recent interest in the area of ferromagnetism has led

to work on systems such as Fe/Cu(6-11), Fe/Au(12), and Fe/Ag(13), and the interesting catalytic properties of Pt-Au alloys have motivated studies of the system Pt/Au(14). These are all systems where $\gamma_f > \gamma_s$, and γ_i is expected to be small, and often positive. For these systems, Bauer's criteria predict Volmer-Weber growth (4).

The present work concerns a system somewhat analogous to Fe/Cu and Fe/Ag in terms of free energies: Rh/Ag(100). The surface free energy of Rh, 2.83 J/m^2 , is more than twice that of Ag, 1.30 J/m^2 (15), and so one would expect three-dimensional clustering of the Rh film here as well. However, we find that the equilibrium configuration of the film falls outside of the three classical modes. Our results indicate that the overlayer structure depends on additional factors which may also be relevant in some analogous systems where controversies have arisen (8,9,11).

II. EXPERIMENTAL PROCEDURES

The experiments are performed in three separate ultrahigh vacuum systems. One chamber is equipped for ultraviolet photoemission spectroscopy (UPS), x-ray photoelectron spectroscopy (XPS), and ion scattering spectroscopy (ISS). A second chamber is equipped for thermal desorption spectroscopy (TDS). Both of these systems have base pressures $\leq 2 \times 10^{-10}$ Torr and are equipped with optics for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), shuttered Rh evaporators, and provisions for CO exposure. The sample manipulators allow for resistive heating, from 120 K up to 1000 K for TDS, and from 300 K to 1000 K for UPS, XPS, and ISS measurements. Scanning Auger measurements are performed in the third chamber, a Perkin-Elmer PHI 600 scanning Auger system, operating in the high 10^{-10} to low 10^{-9} Torr range.

The Ag samples, flat disks approximately 10x10x2mm in size, are cut from the same single-crystal boule, oriented parallel to the (100) face to within $\pm 0.5^\circ$, and polished by standard metallurgical procedures. Sulfur is the only bulk contaminant observable by AES and is removed by repeated argon-ion bombardment at 500 eV ($\approx 2 \mu\text{A}/\text{cm}^2$) and annealing to 800 K. The surface region is determined to be free of sulfur when prolonged heating (1-2 hrs.) at 800 K results in a sulfur signal which is undetectable with AES. After annealing at 800 K, LEED shows the characteristic (1x1) pattern.

Rh is deposited on the sample surface from a resistively-heated, tungsten filament wrapped with 0.25-mm diameter Rh wire (99.8%),

following the design of DeCooman and Vook (16). The Rh source is enclosed in a double-walled, liquid-nitrogen-cooled shroud with a 1.5-cm orifice to allow Rh vapor to escape toward the sample. After thorough outgassing of the filament, the pressure rise in the chamber is about 4×10^{-10} Torr after 60 seconds. No impurities are detectable in the deposited Rh overlayer using either AES or XPS. From AES, the Rh distribution across the sample surface is uniform to within ± 5 -10%. The Rh is removed by argon-ion bombardment after each experiment. The conditions of bombardment are 1 keV, ca. $4 \mu\text{A}/\text{cm}^2$, at 300 K.

III. EXPERIMENTAL RESULTS

Our initial investigations involved monitoring the growth of the film via AES, XPS, $\Delta\phi$ (work function change), and LEED measurements at a substrate temperature of 300 K. It is common to characterize film growth using AES by monitoring the overlayer and substrate signal intensity vs. deposition time (e.g., 17). Accordingly, we measure the Ag_{356} (MNN) and Rh_{222} (MNN) Auger transitions. The results are shown in Fig. 1. It can be seen that the measured peak-to-peak amplitudes of the derivative spectra, plotted as functions of deposition time, are smooth, continuous curves, with no clear changes in slope. The AES data are thus ambiguous in their meaning, since they fail to exhibit the clear straight-line segments, with discontinuities in slope, which are often associated with sequential layer filling (18-20). The absence of such a form in Fig. 1 does not rule out layer-by-layer growth, however (21).

An absolute determination of Rh coverage is difficult. This is because the Auger data (Fig. 1) do not exhibit clear linear segments which demarcate various layers, and because we have no experimental way to monitor the absolute Rh flux from the evaporator. However, we estimate the Rh coverage by assuming that growth is pseudo layer-by-layer at 300 K. The nominal coverages given in Fig. 1 are based on ion scattering results which indicate that after an 80 second exposure to the Rh source the Ag surface atoms are approximately 70% covered. Such a value is consistent with pseudo layer-by-layer or nondiffusive growth processes (22,23) in which the second layer begins to populate before

Figure 1. Variation of the differentiated Rh_{222} and Ag_{356} Auger signal intensities with deposition time during Rh deposition on Ag(100) at 300 K

completion of the first. Also included in Fig. 1, and represented by the solid lines, are the curves calculated for the Ag_{356} signal attenuation and the Rh_{222} signal increase assuming layer-by-layer growth as suggested by Gallon (18). We assume the interlayer spacing in the Rh film is the same as for bulk Rh, 1.90 Å, and use inelastic mean free paths calculated from the equations of Seah and Dench (24). Subsequent coverage values given are based on this data.

Figure 2 illustrates the work function change, $\Delta\phi$, measured from the shift in the low kinetic energy cutoff of the HeI photoemission spectrum. The work function increases smoothly (by ca. 0.5 eV) as Rh, 3 layers, is deposited at 300 K. Measurements of $\Delta\phi$, using a retarding potential method (25), similarly show a smooth increase (ca. 0.7 eV). These data are also shown in Fig. 2. Both measurements are consistent with the higher work function of Rh(100) relative to Ag(100): 5.11 eV (26) vs. 4.65 eV (27), respectively.

Finally, the LEED pattern shows an increase in background intensity with subsequent deterioration and loss of the (1x1) pattern during Rh deposition. The LEED pattern is obliterated at a coverage of ~ 1 Rh layer. There is no evidence of LEED oscillations, as we have observed during growth of Pt films on Pd(100) (28,29,30). These oscillations would be indicative of layer-by-layer growth.

It is often believed that the equilibrium configuration of the overlayer can be attained by annealing a film deposited at room temperature. When a fresh Rh film is heated to 600 K, a very diffuse (1x1) LEED pattern returns, indicating that some ordering of the

Figure 2. Variation of work function during deposition of Rh films at 300 K, as measured by UPS and a retarding potential method

Figure 3. Auger spectra in the energy range 200 to 400 eV
a) Clean Ag(100).
b) Following deposition of ca. 3 layers of Rh at 300 K.
c) As in (b), following heating to 600 K.

overlayer has occurred. The spacing of the large diffraction spots is most consistent with the bulk lattice constant of Ag at low Rh coverages, and with that of Rh at high Rh coverages. In addition, gross changes in the system are evident, as illustrated by the AES data of Fig. 3. XPS data (not shown) indicate a similar result. In both cases, the Rh signal shows a striking decrease in intensity while the Ag signal intensity increases appreciably. Observation of such spectral changes could, in principle, be due to loss of the film via bulk dissolution, and/or agglomeration of the film from flat layers into three-dimensional clusters. However, Rh should be completely insoluble in Ag in this temperature regime (31), and so we do not consider the first explanation to be feasible. Since agglomeration would be expected to occur upon equilibration due to the difference in surface free energies of Rh and Ag, we initially adopted the latter explanation as the more likely. A similar effect has been reported for Pd films on W(110), where the film grows layer-by-layer at room temperature but agglomerates at higher temperatures, resulting in a loss of Pd intensity relative to W (32).

However, additional data are not consistent with the simple hypothesis of Rh agglomeration. Annealing a Rh overlayer not only causes a loss of Rh spectral intensity, but also causes ϕ to drop close to the value of clean Ag, and completely poisons the surface to CO chemisorption. This latter effect is observed by measuring CO uptake at high exposures, 20 L, using both UPS and TDS. In these experiments HeII UPS indicates that CO adsorbs molecularly on all Rh films.

The TDS data are illustrated in Fig. 4. In these measurements the

Figure 4. Thermal desorption of CO

- a) Following exposure of clean Ag(100) to 20 L CO at 120K.
- b) Following deposition of ca. 4 Rh layers on Ag(100) at 120 K, followed by exposure to 20 L CO at 120 K.
- c) Following the experiment of curve (b). Note that at the end of that previous experiment, the sample was heated to 600 K.

sample is exposed to 20 L CO at ca. 120 K, then the temperature is ramped upward while measuring the partial pressure of CO. Curve (a) shows the result for clean Ag(100), and curve (b) shows the result after approximately 4 monolayers of Rh are deposited at 120 K. There is a single major desorption peak at ca. 470 K, which completely disappears after the film is annealed to 600 K, Fig. 4c. Thermal desorption of CO from pure Ag occurs at very low temperatures, below ca. 120 K (33), whereas desorption from Rh is known to take place with maximum rates between 500 and 570 K (34,35,36,37). We thus attribute the peak at 470 K in Fig. 4b to desorption of CO from Rh. We believe that desorption below 200 K in these spectra is largely due to sample heating wires and other manipulator parts, rather than desorption from Ag. These TDS data, combined with the UPS and $\Delta\phi$ measurements, lead us to believe that a Ag layer diffuses to the Rh surface upon annealing, thus poisoning the surface to CO chemisorption.

The data of Fig. 5 support this hypothesis. Figure 5 shows results from an experiment in which the annealed Rh film is slowly argon-ion etched, ≈ 0.02 - 0.03 monolayers/minute, while monitoring the Rh and Ag Auger signal intensities, $\Delta\phi$, and CO uptake. This experiment is performed on a Rh film about 3 layers thick, deposited at 300 K, annealed to 600 K for 15 min., and cooled to 300 K. For the as-deposited and annealed data points indicated, the Auger ratio and workfunction change were measured first, followed by saturation of the surface by a 20L CO exposure and measurement of the CO uptake via the CO-4 σ peak area of the HeII photoemission spectrum. Each successive point there after

Figure 5. Measurements of Rh:Ag Auger ratio (top), work function change (middle), and CO-4 σ peak area (bottom) while a Rh film, ca. 3 layers deep and annealed to 600 K, is argon-ion etched (1keV, 1×10^{-6} Torr Ar) at 300 K

represents the same sequence of measurements taken after argon-ion etching to remove the CO and underlying surface atoms. The depth profiles of Fig. 5 clearly show that the surface has become Ag-rich upon annealing. This Ag layer can be removed to reveal a Rh-rich layer with properties very similar to the fresh Rh film. However, it is evident that the Rh/Ag Auger ratio and CO uptake never quite return to the same values as for the freshly-deposited film at 300 K. This is most likely due to the presence of some Ag mixed in with the Rh, either as a result of the ion-etching or the annealing treatment itself. The higher value of $\Delta\phi$, as deposited at 300K and after sputtering is thought to result from background CO adsorption, which is known to increase the workfunction by as much as 1.2 eV at coverages of 0.60 monolayers on Rh(100)(26).

He-ion scattering experiments provide further support for this picture. We find that dosing an unannealed, Rh-covered surface with CO completely attenuates all the metal scattering signal intensity, i.e., adsorbed CO completely occludes all the Rh sites. Since CO will not stick to Ag at 300 K, this provides a means for detecting the presence of Rh at the surface of an annealed overlayer by looking for a decrease in signal intensity when CO is adsorbed. The results of this experiment, performed using a 1 keV incident ion beam with the system back-filled to a pressure of 5×10^{-6} Torr He, are shown in Fig. 6. These spectra are taken with an apertured (12°) double pass CMA (with appropriate potentials reversed), the ions are scattered through an angle of 150° . The ions are incident on the surface at an angle of 72° with respect to

Figure 6. Ion scattering spectra taken with a rastered ($\approx 1\text{cm}^2$) 1keV ion beam at 5×10^{-6} Torr He

a) Clean Ag(100).

b) Following depositior. of ca. 3 layers of Rh at 300 K.

c) As in (b), followed by exposure to 20 L of CO at 300K.

d) As in (c), following heating to 600 K.

the surface normal. For clean Ag(100), the scattered He ions have an energy of 850 eV, as seen in Fig. 6a. After deposition of about 3 layers of Rh, the spectrum of Fig. 6b is acquired. The scattering from Rh also occurs at 850 eV due to the poor energy resolution of He for high mass atoms. The reduction in scattered intensity is believed to result from some disorder in the film surface, as indicated also by LEED measurements, and/or attenuation from gas adsorption rather than a large difference in scattering coefficients or neutralization efficiencies. When this surface is exposed to CO, the peak at 850 eV disappears as shown in Fig 6c. The peak at 380 eV in this spectrum is a result of He scattering from the oxygen of the adsorbed CO molecules. The ISS spectrum after annealing to 600 K is shown in Fig. 6d. It is clear that there is a large recovery of the peak at 850 eV. Dosing again with 20 L of CO and repeating the scattering experiment has no effect on the peak height, indicating that all the Rh sites have been completely covered with Ag. This is also suggested independently from the absolute peak intensities of Fig. 6a and 6d, which are identical within experimental error. These data show that there is Rh exposed at the surface of the film deposited at 300 K, and that Ag covers the surface upon annealing to 600 K. This is in complete agreement with the results from TDS.

We estimate the thickness of the top Ag layer to be one to two atoms. This depth is consistent with the conditions required to sputter through the top Ag layer, assuming a sputtering yield of unity. This value is also suggested, independently, from the ratio of Rh/Ag Auger intensities, 0.10, which we obtain after annealing very thick Rh layers,

about 16 layers deep. For one and two monolayers of Ag on Rh(100), this ratio is known to be 0.25 and 0.09, respectively (33). The LEED data indicate that, at low Rh coverages, the top Ag layer adopts approximately the same lattice constant as bulk Ag (and the Rh must follow suit), whereas for thick Rh films, both the Rh and Ag adopt the two-dimensional lattice constant of bulk Rh.

Several experiments, including AES, ISS, and TDS, have been used to ascertain more precisely the conditions under which Ag moves to the Rh surface. The AES data are shown in Fig. 7, where the sample is heated at a rate of 1-2 K/sec with successive 60 second pauses at each temperature to record the Auger spectrum. The Rh:Ag Auger ratio is shown as the ordinate. The abrupt decrease in this ratio reflects the onset of Ag migration to the surface. It can be seen that when the initial coverage of Rh is about 1 monolayer, Ag migration occurs at ca. 360-380 K, whereas at higher coverages (up to 4 monolayers) it begins at ca. 420 K. Another interesting aspect is the fact that the final ratio of Rh:Ag intensities always approaches the same value, 0.1, for all initial Rh coverages above approximately 1 monolayer.

ISS can be used to study this phenomenon as well, by exploiting the ability to mask ion scattering from the surface Rh atoms using adsorbed CO. This is accomplished by saturating a fresh Rh deposit with CO, and then monitoring the intensity of the He ion scattering peak at 850 eV as a function of temperature. The result of this experiment is shown in Fig. 8, for an initial Rh coverage of ca. 3 monolayers. This measurement indicates that Ag begins to appear at the surface at about 400 K,

Figure 7. Variation of Rh:Ag Auger ratio as a function of sample temperature, for several initial coverages of Rh as deposited at 120 K

Figure 8. Intensity of the He ion scattering peak at 850 eV as a function of temperature (1 keV at 5×10^{-6} Torr He, 1 cm^2 raster)

Figure 9. Thermal desorption of CO from Rh films deposited at 120 K and exposed to 20 L CO at 120 K

Each curve represents a different initial coverage of Rh.

slightly lower than the onset determined with AES. This is most probably due to the higher surface sensitivity of the ISS experiment.

It is useful to compare the ISS and AES data with the TDS results, shown as a function of Rh coverage in Fig. 9. The onset of desorption for the 3-layer film of Fig. 9, 400 K, is identical within experimental error to the temperature at which the ion scattering intensity first increases, and the peak temperature corresponds to the inflection point of the ISS curve of Fig. 8. Combining the AES, ISS, and TDS data allows us to conclude that the desorption of CO is not a simple unassisted event, but rather CO is being displaced by diffusing Ag. These observations explain the low temperature at which the CO desorption peak maximum occurs, 30 to 100 K lower than for the surfaces of bulk Rh (34,35,36,37).

The temperature of CO desorption shifts upward as Rh coverage increases in Fig. 9. Both the desorption onsets and the desorption peak maxima move to higher temperatures. The TDS measurements reveal that these increases must reflect an increase in kinetic limitations for diffusion by Ag, in the case of the thicker film. This suggests that the mechanism for Ag diffusion is somewhat different at low Rh coverages than at higher Rh coverages. A reasonable scenario is one in which bare patches of silver are exposed at low Rh coverages, so the migration of Ag to the Rh surface involves simple lateral migration. However, at higher Rh coverages the Ag must break through a more contiguous Rh film, and this is more difficult. This mechanism is illustrated schematically in Fig. 10.

Figure 10. Schematic model of Ag diffusing to coat the Rh film

a) Low Rh coverages.

b) High Rh coverages.

Auxiliary measurements, obtained by transferring the sample to a scanning Auger microscope (SAM), lend support to the diffusion mechanism described in Fig. 10. A fresh Rh film, ca. 16 layers deep, is deposited and annealed to 600 K for 30 minutes in order to bring the Ag to the surface. The sample is then transferred (in air) to a SAM instrument. Initial measurements show that after exposure of the sample to atmosphere, the surface is predominantly Rh, with only a small amount of Ag still detectable. Sulfur and carbon are also present. Apparently, the Rh must have a higher affinity for the contaminant species, and the Ag is thus driven back off the surface.

Only after removal of the contaminants by ion etching does Ag migrate back to the surface. This migration is again found to occur at about 380 K. We are fortunate, in that the secondary electron yields for Rh and Ag are sufficiently different that the Ag can be monitored visually in this device as it migrates to the surface. A series of time-lapse micrographs, indicating the evolution of the Ag layer at the surface, is shown in Fig. 11. Fig. 11a is a micrograph of the carbon- and sulfur-contaminated surface while it is held at 380 K. No changes in surface composition are evident even after several hours at this temperature. When the surface is lightly ion-etched to remove the contamination, Ag spreads almost immediately out onto the surface. This is evident in Fig. 11b, which is taken in the first 60 seconds after turning the ion beam off. The sample temperature is maintained constantly at 380 K. The diffusing Ag shows up as light spots on the darker Rh background. The changes are even more pronounced in Fig. 11c,

Figure 11. Electron micrographs of a thick, ≈ 16 layer, Rh film

Sample temperature is held at 380 K.

- a) Carbon and sulfur contaminated surface (2510x).
- b) As in (a), ion-etched to remove the carbon and sulfur, 60 seconds after turning off the ion beam (2510x).
- c) As in (b), 15 minutes after turning off ion beam (2510x).
- d) As in (c), magnification of 508x.

taken 15 minutes after sputtering. It must be noted that the changes in the micrographs are due to changes in elemental composition of the surface layers, not changes in topography.

The diffusion of Ag appears to begin at randomly-dispersed point sources and then slowly spread out over the surface. The Ag does not seem to emerge uniformly, as would be envisioned for surface segregation from an equilibrium alloy. Auger spectra taken from the Ag patches indicate again that the Ag is only one to two atoms deep. A lower-magnification picture of the same area, Fig. 11d, shows that the size of Ag islands are mostly uniform, except for a few larger patches. The larger Ag islands could result from faster diffusion through larger defects, or possibly through thinner areas of the film. The firm conclusion that we can reach, however, is that the Ag appears to spread outward from randomly-distributed, point sources, rather than emerging uniformly across the surface.

Some insight into the structure of the Rh films, and the way in which this structure depends upon temperature, is provided by XPS. These data are shown in Fig. 12. It can be seen that the Rh binding energy (B.E.) increases with deposition time at 300 K, which undoubtedly reflects the increase in average atomic coordination of Rh atoms as the bulk configuration is approached (38). This trend is evident for submonolayer to ~ 3-4 monolayers of Rh. The Ag binding energy decreases continuously, in a way which is independent of the film's thermal history. The decrease of the Ag B.E. must be due to an increase in the contribution from the less-highly-coordinated Ag at the interface or at

Figure 12. Variation of core-level binding energies (B.E.), measured with XPS using Mg- K_{α} radiation, for both Rh and Ag as a function of deposition time during growth of Rh films

the surface, and concurrent attenuation of signal from the bulk Ag as Rh coverage increases. A more puzzling result is the fact that there is no measurable change in Rh B.E. when a Rh overlayer, deposited at 300 K, is annealed to 600 K. This is true for low (< 1 layer) as well as high coverages (3-4 layers) of Rh. On the other hand, when a Rh film is deposited at 600 K, the shift in B.E. for fixed deposition time is smaller than at 300 K. These results are shown also in Fig. 12. In other words, the B.E. shift depends quite strongly on the history of the film; annealing to 600 K has a much different effect than depositing at 600 K. There are two possible explanations for this. One is that the composition of the Rh layer is different in the two cases. More intermixing of Ag with Rh may occur when Rh is deposited at the higher substrate temperature, thus leading to a decrease in the Rh B.E. This intermixing could be due to the high mobility of Ag at 600 K, which allows it to constantly migrate toward the surface and be buried by the incoming Rh atoms. Another explanation is that the morphology of the films is different in the two cases. If the film deposited at 300 K is significantly rougher than the one grown at 600 K due to limited Rh diffusion at the lower substrate temperature, this would be consistent with the data as well. However, one would then have to conclude that annealing a rough film to 600 K does not allow it to become more smooth. This would be reasonable, since cooperative, large-scale rearrangement of an already-rough film would undoubtedly be relatively difficult, and may simply not occur on the time scale of our annealing experiments. Homoepitaxy experiments may be a possible means of ascertaining

experimentally whether Rh is much more mobile at 600 K than at 300 K.

The XPS data lead us, then, to conjecture that the content of the middle Rh layer may depend upon the film's history. To test this hypothesis, depth profiles (sputtering rate $\approx$ 0.1-0.2 monolayers/minute) were performed with AES, following different thermal treatments. Fig. 13 shows the results of these profiles for films about 3 layers thick. There is obviously little difference between the profile of the film heated to 600 K, Fig. 13b, or that of the film deposited at 600 K, Fig. 13c. The change in composition needed to bring about the observed difference in Rh B.E. is unknown, and it may be so small that we cannot differentiate between the two in the profiles. In addition, the ion beam used in the depth profiling tends to roughen and mix the interface, making it difficult to distinguish small changes in the concentration profiles. However, we conclude that the differences in film composition, if present, are relatively small (less than about 20%). The Rh signal remaining after 60 minutes of sputtering can be explained by the overlap of the Rh₃₀₂ transition (used to monitor the Rh concentration) and the Ag₃₀₁ transition, and/or Ar-ion mixing or knock-on from the sputtering process.

If there is intermixing between the two metals in the middle layer, we do not believe that this reflects significant alloy formation. We have measured the angle-integrated, HeII, UPS spectra for the Rh/Ag films, both before and after annealing. These spectra are shown in Fig. 14. Alloying may be accompanied by a mixing or hybridization of states which can give rise to new features, or shifts in the existing features

Figure 13. Depth profiles, using the peak heights of the differentiated Rh_{302} and Ag_{356} Auger transitions, for Rh films which have undergone various thermal treatments

- a) 3 layers of Rh deposited at 300 K.
- b) 3 layers of Rh deposited at 300 K, then annealed to 600 K for 15 minutes.
- c) 3 layers of Rh deposited at 600 K.

Figure 14. Angle-integrated HeII photoemission spectra of the 4d band region of the valence band, taken with a He resonance source

- a) Clean Ag(100).
- b) Following deposition of ca. 3 Rh layers at 300 K.
- c) As in (b), following heating to 600 K.
- d) As in (c), sputtered to remove the top Ag layer.

of the valence band density of states. Such effects have been observed, for instance, in the systems Pd/Cu (39,40,41), Pd/Ag (27), and Ni/Cu (42). The data of Fig. 14 show that the spectra for Rh/Ag are just a superposition of the bulk Rh and Ag d-band spectra, both before and after annealing. These data are not to be taken as unequivocal evidence against alloy formation since alloying may result in only small changes in the density of states, especially for dilute alloys, and may not be observable in these spectra.

Another question about the structure of the film is whether any Ag is present at the surface following Rh deposition at 300 K, i.e., before any annealing. None of the data presented until now would be sensitive to small amounts of Ag at the surface under these conditions, including the ISS. In Fig. 13a, however, the profile of the unannealed Rh film shows an initial decrease in the Ag intensity, indicating some small surface enrichment in Ag. This shows that even at room temperature, Ag has enough mobility to diffuse (slowly) onto the top of the Rh. However, the rate at which the Rh film is grown and the moderate temperature of the substrate serve to kinetically limit the diffusion process, and the equilibrium configuration is only reached on a reasonable time scale after annealing the system.

A final question about the nature of the film is, what is its three-dimensional structure? Is it largely smooth, or does the Rh form three-dimensional crystallites? The best available answer to this question is given by the AES data shown in Fig. 15. As mentioned earlier, the Rh/Ag Auger ratio for an annealed film of ≈ 16 layers is 0.1. This same ratio

Figure 15. AES ratio during film deposition at 300 K ($\approx$ 3-layers) and 600 K ($\approx$ 9-layers)

is obtained for all films thicker than 2-3 layers, whether they are annealed to 600 K after deposition, or grown at 600 K. This is evident in the data of Fig. 15. For films grown at 600 K this ratio plateaus at a coverage of about 3-4 Rh layers. For a 16-layer film the coverage is ≈ 4 times that required to completely attenuate the substrate signal, and Ag is detected only after the film is annealed. For the unannealed, 3-layer film the Ag signal intensity is still 20% of the clean substrate signal, yet after annealing the Rh/Ag ratio is identical to that of an annealed 16-layer film. If the Rh does agglomerate upon heating, the Rh:Ag ratio should still increase with increasing Rh coverage, only at a lesser rate, and plateau only when the crystallites have grown large enough to coalesce and completely attenuate the substrate Auger signal. It is difficult to envision how the Auger ratio for 3- and 16-layer annealed films could possibly be identical, if significant agglomeration occurs upon annealing. However, for a flat Rh overlayer with a layer of Ag on the surface, the constant Auger ratio for the large range of Rh coverages is more easily explained.

This second explanation of the identical Auger ratio is also reasonable, in light of the attenuation of Ag Auger electrons emitted from the substrate. Assuming the thickness of an ordered, flat Rh monolayer to be bounded by the values for the interlayer spacings of bulk Rh and Ag (100) planes, 1.90 Å and 2.05 Å respectively, and using an inelastic mean free path of 7.0 Å, the attenuation length of the Ag_{356} electrons should be approximately 4 monolayers. A Rh film of 3-layers which has been annealed to bring a layer of Ag to the surface results in

a total coverage of 4 monolayers, approximately the attenuation length of the Ag_{356} Auger electrons. This would indicate that the majority of the electrons contributing to the measured Auger signals originate from layers above the Ag substrate/Rh interface for all Rh coverages greater than 3 layers. Therefore if the Rh layers remain flat, and the concentration of Ag dispersed throughout the Rh and at the surface remains essentially constant, for all Rh coverages, a constant Rh/Ag ratio would be expected for films greater than about 3 layers. This seems to be a more acceptable explanation for the constant Auger ratio than agglomeration. Our AES data thus seem to support the formation of a flat Ag-Rh-Ag sandwich.

IV. DISCUSSION

A. Structure of the Metallic Film

The equilibrium structure of a Rh film on Ag(100) is that of a Ag-Rh-Ag sandwich. The top Ag layer is only one or two atoms deep, and it completely blankets the Rh. The energetic driving force for this silver migration is undoubtedly the reduction in the system's surface free energy, which is accomplished by this very thin layer of Ag. However, the Ag layer is also highly strained, especially at high Rh coverages, since our LEED data indicate that it adopts the lattice constant of the Rh substrate, 8% lattice mismatch. This creates an unfavorable energy term in the total energy balance, a term which apparently dominates at coverages above one or two atomic layers of Ag. This strain energy may also prevent more Ag from moving to the surface.

It is informative to compare our results with work of Peebles et al. (33) in which Ag films on Rh(100) were studied. Those authors find that Ag grows layer-by-layer up to at least three atomic layers at 300 K, and follows Stranski-Krastanov growth at 640 K, close to the annealing temperature of many of our experiments. They report that clustering begins during Stranski-Krastanov growth at coverages in excess of one monolayer. They also find that the film grows epitaxially up to a coverage of one monolayer at 300 K, but reconstructs into a pseudohexagonal lattice at higher coverage. Both of these findings suggest that Ag coverages above one monolayer cannot accommodate the 8% lattice misfit with the Rh substrate, and either reconstruct (at 300 K)

or agglomerate (at 640 K) to relieve the strain. To the extent that our Rh films are electronically and structurally similar to their Rh(100) substrate, their results can be extrapolated to our system. This suggests that the top layer of our sandwich is probably limited to a single Ag atom in thickness.

The middle layer of the sandwich is mainly Rh. The bimetallic phase diagram (31) indicates that a dilute Rh-Ag alloy, consisting of ≤ 5 atomic % of Ag, exists at room temperature, and so there may be a small amount of Ag truly dissolved in the Rh layer. However, this possibility is disfavored by the results of Peebles et al. (33), who find no evidence for dissolution of Ag into Rh(100), even at temperatures up to 1370 K. Presumably, the detection limit in their AES experiments is on the order of 1 or 2%. There may be some pure Ag phase trapped in our Rh films, especially those grown at elevated temperatures. This is because the Ag tends constantly to migrate toward the surface as the film is being grown at elevated temperature, and some of it may become buried within the growing film.

We believe that the substrate is pure Ag, with no dissolved Rh. We have no experimental data to this effect, but the phase diagram (31) indicates that less than 0.5 atomic % of Rh is soluble in Ag at room temperature. Thus, we propose that the layers of this sandwich are rather pure, with some metallic intermixing in the middle layer, but none in the top and bottom layers.

For the reasons given in Section III, we believe that the Ag-Rh-Ag sandwich is essentially flat. In this case, Rh films thicker than one

monolayer must develop misfit dislocations in order to accommodate the 8% lattice mismatch between the Rh and the Ag. The misfit dislocations presumably account for the diffuse nature of the (1x1) LEED pattern which we observe for the annealed films, even for thick Rh sandwiches.

The morphology of the Rh films grown at 300 K, where silver migration is slow on the time scale of our experiments, is also questionable. The sharp (1x1) LEED pattern of the substrate is obliterated after 1 layer of Rh is deposited at room temperature, which may indicate that the Rh atoms are randomly and uniformly distributed over the surface. If significant agglomeration occurred under these conditions, one might expect the underlying Ag substrate to give a residual LEED pattern even at much higher Rh coverages. It may be that the film grows via random deposition of Rh atoms, and that thermal diffusion is slow at 300 K. In this case, the growing film would be rough, yet would have some layer-by-layer quality, especially for the first 2-3 monolayers. The observation of layer-by-layer quality in films grown at temperatures where single-atom diffusion is negligibly slow has been a topic of some recent discussion (23,29,30,43-45).

B. Mechanism of Silver Migration

The data presented clearly show the ability of Ag to migrate to the surface of a Rh film, the kinetics of this process depending on the substrate temperature and the film thickness. The exact mechanism which leads to the sandwich structure is not clear. It is well known that binary alloys often show a tendency for surface enrichment or segregation

of one of its components. Many theories exist which can be used to predict the surface segregation of transition metal alloys (46,47). These theories predict the segregation of Ag in the Rh/Ag system. Therefore it is possible that the sandwich forms as a result of the segregation of Ag from a dilute Rh-Ag alloy. However, SAM results indicate that the Ag diffusion appears to begin at randomly-dispersed point sources and then slowly spreads out over the surface. The Ag does not seem to emerge uniformly as would be envisioned for surface segregation from an equilibrium alloy.

There exists a more plausible explanation for the development of the Ag-Rh-Ag sandwich, as illustrated previously in Fig. 10. The migration of Ag at low Rh coverages may involve simple lateral migration of Ag atoms from bare patches of the substrate. This is easy to envision. However, at higher Rh coverages the Ag must break through a more contiguous Rh film. For these higher Rh coverages it is possible that Ag arrives at the surface via diffusion through defects which may exist in the overlayer. We know that the film is disordered when deposited at 300 K and annealing restores a LEED pattern. However, the LEED pattern is diffuse, possibly from a large population of defects. We also know from the depth profile of Fig. 8a that there appears to be some Ag on the surface of the film even before annealing. This migration of Ag at 300 K, in addition to the development of misfit dislocations in the film could be responsible for creating channels in the Rh layers through which more Ag diffuses at higher temperatures. The population of these channel defects would then be expected to be larger for films grown at 600 K due

to the continuous diffusion of Ag at this temperature. The XPS results which indicate a lower average atomic coordination for the Rh atoms for films grown at 600 K lend support to this statement. These results lead us to believe that diffusion of Ag (driven by the large difference in surface free energies) through defects created in the Rh film is the dominant mechanism which leads to the formation of the sandwich structure.

C. Comparison with Other Work

Ours is not the first evidence for surface enrichment of Ag in a Rh/Ag system. Anderson et al. (48) and Rouco and Haller (49), working with silica-supported, Rh-Ag particles, found evidence of Ag on the surface of Rh particles in a thin layer, perhaps only one atom thick. Their x-ray diffraction results suggest the presence of separate Rh and Ag phases. These observations are similar to our own.

We have found only two other cases of "sandwich" structures in the literature. Chen et al. (50) working with Ag on Pb(111) and Rawlings et al. (51) working with Ag on Pb(111) and Cu on Pb(111) report results similar to our own. In both cases a monolayer of Pb is found to be present at the surface after deposition at room temperature of very thick layers, 2000 Å of Ag (50) and 100 Å of Ag or Cu (51). These are metals which should be totally immiscible in the temperature range under consideration. Similar to the Rh/Ag system, the driving force in these cases is thought to be the large difference in surface free energies (the substrate being the much lower surface-free-energy material), and

immiscibilities of the overlayer and substrate metals. These findings indicate that for metal-on-metal systems of this category, sandwiches may be a general phenomenon and should be considered in addition to the three long-standing modes of equilibrium growth.

We believe that this phenomenon may not be restricted to these three systems. There are several instances where the growth mode of analogous systems is not well understood (8,9,11,14). In these instances the substrate is often assumed to be a rigid, stationary template, with the structure of the overlayer depending only on overlayer atom mobility, electronic interactions, lattice mismatches, and surface energy constraints. However, we have shown that substrate atom mobility can provide additional pathways to satisfying thermodynamic requirements.

V. CONCLUSIONS

We have found that the mode of growth of the Rh/Ag(100) system does not follow any of the three classical growth modes, i.e., Frank-van der Merwe, Stranski-Krastanov, or Volmer-Weber. In a system such as this where the free energy of the film is greater than that of the substrate, and the free energy of the interface is thought to be small, Volmer-Weber growth is expected. Traditionally it is thought that the film will grow as three-dimensional crystallites to expose a large area of the substrate and thus keep the surface energy at a minimum. However, if the mobility of the substrate atoms is sufficient to allow diffusion which results in a lowering of the surface energy, agglomeration need not be invoked. We believe that this is the case for the Rh/Ag(100) system which leads to the formation of a Ag-Rh-Ag sandwich structure. The essential feature in this system is the substrate atom mobility. Growth in this manner may be typical for immiscible systems and those with limited solubility which also possess large differences in surface free energies, the extent of substrate diffusion being governed by the magnitude of these energy differences and solubilities.

We would also like to add that since this publication, molecular dynamic simulations for the Rh on Ag(100) system have been completed by Raeker et al. (52). These simulations indicate that for the low coverage regime an alternative mechanism for the silver migration may consist of simple site exchange between the Rh and Ag which results in Rh being incorporated in a film below a Ag layer.

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PAPER II:

Au FILMS ON Pd(110): Pd INDUCED CO DESORPTION FROM Au AND
COVERAGE DEPENDENT (1X2) AND (1X3) Au RECONSTRUCTIONS

AU FILMS ON Pd(110): Pd INDUCED CO DESORPTION FROM Au AND
COVERAGE DEPENDENT (1X2) AND (1X3) Au RECONSTRUCTIONS

P. J. Schmitz, H. C. Kang, W. -Y. Leung, and P. A. Thiel

Department of Chemistry and Ames Laboratory
Iowa State University
Ames, Iowa 50011

ABSTRACT

We present the results of a study of Au films grown on Pd(110) in the 1 to 10 monolayer regime. The growth and reconstruction of the Au films are followed via LEED, AES, and carbon monoxide TDS. The films are deposited at a substrate temperature of 130 K, followed by annealing at temperatures up to 800 K. For the first few Au layers, TDS experiments reveal low temperature desorption features at 225 and 190 K which we associate with CO desorption from the Pd modified Au surface. For Au coverages below 2 monolayers, only a (1x1) overlayer structure is observed with LEED over the entire temperature range studied. At 2 monolayers of Au, the films reconstruct irreversibly to a (1x2) structure at temperatures slightly over 300 K. With increasing coverage and at temperatures slightly over 300 K, the half-order beams split continuously, and eventually a full (1x3) structure develops by 4 monolayers. The development of the low temperature CO desorption features, the (1x2) and (1x3) coverage dependent superstructures, and the continuous spot splitting are addressed. This is the first observation of CO adsorption on Au at temperatures over 125 K, and the first report of the reconstruction of an fcc metal film whose clean (bulk) surface reconstructs, grown on a nonreconstructed (110) substrate.

I. INTRODUCTION

The phenomenon of surface reconstruction has been an area of interest to surface scientists for quite some time, as evidenced by the large wealth of experimental (1-21) and theoretical work (22-26). It is well known of the fcc metals Au, Pt, and Ir, that the (100) and (110) surfaces of all three metals, and the (111) face of Au, reconstruct to form atomically different two-dimensional periodicities than those predicted by simple termination of the bulk structure (27, and Ref. therein). Since the rearrangements in these systems are known to be limited to the first few atomic layers (27, and Ref. therein), it is of fundamental interest to study thin films of these metals, to determine under what conditions the films may exhibit their bulk-like reconstructions. An early study by Palmberg and Rhodin (28), showed that for Au films on a (100) substrate only a few monolayers are required to support the Au bulk-like reconstruction. Since Palmberg and Rhodin's initial work (28), other studies of the growth of Au and Pt overlayers have been completed (29-40). However, all workers to date, except Fenter and Gustafsson (40), have used the more atomically-smooth fcc (111) and (100) crystal faces. There are no reports of the reconstruction of Au, Pt, or Ir films grown on fcc (110) substrates.

The (110) faces of Au, Pt, and Ir are known to exhibit (1xn) "missing row" reconstructions, where n can take the values of 2,3, and even higher integers (3-5,7,9-25,27). It is the objective of this study to determine whether and under what conditions Au films may exhibit their

bulk-like reconstructions when grown on a (110) substrate of another fcc metal which does not reconstruct. The clean (110) surface of bulk Pd, our substrate, is stable against reconstruction (41,42). For the (110) surface of bulk Au, (1x2) reconstructions are most frequently reported in the literature (16-21,24,25,27), but (1x3) structures have also been reported (3,7,15). We observe both of these structures for the Au films, their formation having a direct dependence on the film thickness.

II. EXPERIMENTAL PROCEDURES

The experiments are carried out in an ultrahigh vacuum chamber equipped with a shuttered Au evaporation source, a shuttered cylindrical mirror analyzer for Auger electron spectroscopy (AES), shuttered optics for low-energy electron diffraction (LEED), and provisions for controlled gas exposure. Base pressures are below 2×10^{-10} Torr. The LEED patterns are monitored with a video imaging system described previously (43).

The Pd crystal is oriented parallel to the (110) face to within $\pm 1^\circ$, and polished by standard metallurgical procedures. The crystal is cleaned by repeated cycles of argon-ion bombardment (1keV, $1.5\mu\text{A}/\text{cm}^2$) at 300 K, followed by cycling in oxygen to remove carbon and heating to 1100 K to desorb residual oxygen. The surface cleanliness is determined by CO thermal desorption which gives spectra equivalent to those reported previously for a carbon free surface (44). The sample is mounted by spotwelds to two Ta support rods which in turn are connected via copper braids to current feedthroughs in a liquid nitrogen reservoir. This configuration allows the sample temperature to be varied from 130 K up to 1100 K by resistive and radiative heating of the crystal. The crystal temperature is monitored by a W-5% Re/W-26% Re thermocouple spotwelded to the back of the sample. The temperature is controlled through a feedback circuit designed by Herz *et al.* (45).

Au is deposited on the sample surface from a resistively-heated tungsten filament wrapped with 0.50mm diameter Au wire (99.999%), following the design of DeCooman and Vook (46). The Au source is

enclosed in a double-walled, liquid-nitrogen-cooled shroud with a 1.5 cm orifice to allow Au vapor to escape toward the sample. After thorough outgassing of the filament, no pressure rise above background (2×10^{-10} Torr) is observed during evaporations. In order to obtain reproducible evaporation rates, the evaporator filament temperature is regulated through the same feedback circuit designed by Herz et al. (45), using a W-5% Re/W-26% Re thermocouple. The thermocouple junction is sandwiched in a small piece of Ta foil to prevent Au contamination of the junction, and then the Ta foil is spotwelded to the tungsten filament approximately 2 cm from the Au load. This allows the filament temperature (at the thermocouple junction) to be regulated at approximately $1000 \pm 1^\circ \text{K}$. Au has a melting point of 1340 K, and a vapor pressure of about 10^{-9} Torr at 1000 K (47). This setup results in reproducible evaporation rates on the order of 1 monolayer per minute. This evaporation rate implies $P_{\text{Au}} \sim 10^{-8}$ Torr, which is not unreasonable since the Au source is undoubtedly hotter than the thermocouple. No impurities can be detected by AES after deposition of the films. Also using AES, the Au distribution across the sample surface is found to be uniform to within $\pm 5\%$. The Au is removed by argon-ion bombardment after each experiment. The conditions of bombardment are 1 keV, ca. $1.5 \mu\text{A}/\text{cm}^2$, at 300 K.

The Au films are deposited by exposing the Pd crystal, held at the desired deposition temperature, to the Au vapor flux. The resultant film thickness is determined by AES. After deposition, the sample is slowly heated to a desired temperature, held for 20 seconds at constant temperature to allow equilibration, and then quenched below 200 K where

the LEED pattern is observed. The sequence is then repeated for the next annealing temperature. Diffraction spot profiles are recorded and processed with the video-LEED system (43).

We also use CO thermal desorption spectroscopy (TDS) as a means of calibrating Au coverage. However, due to our experimental setup we must use a rather unconventional method to acquire the desorption spectra. In the traditional TDS experiment, the crystal is held at low temperature and exposed to the gas of interest. A thermal ramp is then initiated and the evolution of the gas phase desorbing species is followed via a mass spectrometer. In our desorption experiments the sample manipulator poses a small problem. The flexibility, required for a tilt mechanism incorporated in the manipulator, requires that bulky Cu-braids be used to provide the thermal and electrical contact to the crystal. In addition, the ionizer for the mass spectrometer is not shielded so as to accept species desorbing only from the crystal surface, i.e., it has no directional aperture. In the CO desorption spectrum from clean Pd(110) we observe a large peak centered at ≈ 150 K which tails off to temperatures over 200 K. Since CO is known to desorb from Pd(110) at temperatures over 300 K (44), we attribute this spike to desorption of species from the Cu-braids and heating wires. In order to reduce contributions to the desorption spectrum from the Cu-braids and heating wires during CO-TDS experiments, we use a simple procedure. The sample is cooled to 130 K, the lowest temperature attainable with this manipulator, and is given a saturation exposure of CO, 6 Langmuir (L). The temperature of the crystal is slowly raised to 170 K and held for 1

minute. The crystal is then cooled back to 130 K, and the desorption spectrum is collected over the entire temperature range. This low temperature anneal results in desorption of most species originating from the Cu-braids and heating wires and substantially cleans up the low temperature region of the desorption spectrum. This procedure then allows the identification of any desorption features which may appear above 180 K.

III. EXPERIMENTAL RESULTS

A. Coverage Calibration

Our initial investigations involved monitoring the Au films using AES and LEED to determine the coverage, mode of growth, and overlayer structure of the deposited films. It is common to characterize the growth of the overlayer using AES by monitoring the substrate and overlayer Auger intensities as a function of deposition time (e.g., 48). Accordingly we have measured the $\text{Pd}_{330}(\text{MNN})$ and $\text{Au}_{69}(\text{NVV})$ Auger transitions. Various methods have been used when plotting these signals (48-51), all of which attempt to discern small discontinuities in slope which are often associated with a Frank-van der Merwe (layer-by-layer) growth mechanism (52). Our results, shown in Fig. 1, are plotted as the peak-to-peak amplitude of the Au and Pd derivative spectra, and as the ratio of the overlayer to substrate signal intensities vs. deposition time. The peak-to-peak amplitudes plotted as functions of deposition time, Fig. 1(a), are smooth, continuous curves, with no clear changes in slope. When these data are plotted as the ratio of overlayer to substrate signal intensities vs. deposition time, Fig. 1(b), slight discontinuities in the slope appear to be present. We have drawn straight line segments through the data of Fig. 1(b) to accentuate the points where slight breaks in the slope appear to occur. These discontinuities in slope are found for deposition times of 100 and 200 seconds, corresponding to Au/Pd ratios of 0.45 and 1.00 respectively. These data can be interpreted as an indication of layer-by-layer growth

Figure 1. Variation of the Au₆₉(NVV) to Pd₃₃₀(MNN) Auger signals versus deposition time
 a) Plotted as the peak-to-peak amplitudes of the Au and Pd derivative spectra.
 b) Plotted as the ratio of the peak-to-peak amplitudes of the Au and Pd derivative spectra.

(at least for the first two layers), the breaks in the curve indicating the completion of the first and second monolayers. However, these breaks are very subtle, especially the first break. In fact, the data of Fig. 1(b) could be fit just as well by a continuous curve through the data points. The absence of clear linear segments in the AES data also does not rule out layer-by-layer growth (37).

As a cross-check, we have estimated the Au to Pd ratio for 1 and 2 monolayer films using equations which describe the substrate and overlayer signal intensity as a function of film thickness (53). For this analysis we use inelastic mean-free-paths for the $\text{Au}_{69}(\text{NVV})$ and $\text{Pd}_{330}(\text{MNN})$ Auger electrons of 4 Å and 7 Å, respectively (54,55), and handbook spectra for a measure of the peak-to-peak intensity ratio for bulk Au and Pd (56). Using this method we obtain values for the ratio of Au to Pd of 0.5 for the first monolayer and 1.1 for the second monolayer. These values agree well with the subtle breaks envisioned in the AES data of Fig. 1(b), although determining breaks in these curves can tend to be subjective (57-59), and inelastic mean-free-paths used in these cross-check calculations may not be very reliable.

Because of ambiguities in the above measurements, we have undertaken measurements of CO thermal desorption yield for the Au/Pd system to assist in coverage calibration. The interaction of CO on Au surfaces is known to be very weak, and adsorption does not take place on Au(110) even at temperatures as low as 125 K (60). However, CO binds quite strongly to Pd and desorbs at temperatures exceeding 300 K (44). Therefore, the addition of Au ad-atoms should block the strongly interacting Pd sites

and thus suppress desorption of CO above room temperature. By looking for a minimum in the CO desorption yield above 300 K as Au coverage increases, one should get an indication of when the Pd lattice is completely covered by a Au monolayer. That is, the minimum in the yield will indicate the completion of the first layer if the film truly grows layer-by-layer. A procedure of a similar nature has been reported previously for Ag on Ni(100) and Ni(111) (61).

We measure the CO desorption yield from Pd(110) in the region above 300 K, as the Au coverage increases. In these measurements the crystal is cleaned and the temperature is lowered to 130 K. The crystal is then rotated in front of the evaporation source, and the shutter is opened exposing the crystal to the Au vapor flux. Following Au deposition, an Auger spectrum is recorded and the $Au_{69}(NVV)$ to $Pd_{330}(MNN)$ ratio of peak-to-peak intensities is measured. The crystal, still at 130 K, is then given a 6 L exposure to CO to saturate all adsorption sites. The sample is pre-annealed to 170 K to decrease desorption contributions from the heating wires as described earlier, cooled back to 130 K, rotated in front of the mass spectrometer and the desorption spectrum recorded. This procedure is repeated for a series of increasing Au coverages, and the desorption peak areas for the Pd-CO features ($T_{\text{desorption}} > 300$ K) are measured.

The results of the CO desorption yield from Au-covered Pd(110) are displayed in Fig. 2, as the normalized CO peak area (for $T_{\text{desorption}} > 300$ K) vs. the Au/Pd Auger ratio. There is a very drastic drop in the CO desorption yield as Au coverage increases, and the yield reaches a

Figure 2. Plot of the normalized CO-desorption yield from Pd(110) as a function of increasing Au coverage

All measurements are taken following a 6L exposure to CO at a substrate temperature of 130 K and subsequent treatment as described in Section II.

minimum when the Au/Pd Auger ratio is 0.40 to 0.50. The non-zero minimum for the desorption yield arises because of contributions to the desorption spectrum from the sides and back of the crystal which can not be suppressed in the desorption experiments. When the value for the minimum in the CO desorption yield is compared to the AES results, this minimum corresponds very well with the apparent first break in the Auger curve which occurs at a Au/Pd ratio of 0.45. The good agreement between these two independent measurements permits the identification of the first Au monolayer. Subsequent coverages quoted are based on these data.

B. Low Temperature Desorption Features

While conducting the CO desorption yield measurements on the Au overlayers, low temperature features appear and intensify as the Au coverage is increased. Presented in Fig. 3 are some CO-TDS spectra displayed as a function of Au overlayer thickness. Shown in Fig. 3(a) is the CO desorption spectrum from the clean Pd surface. This spectrum is equivalent to previously reported desorption spectra from clean Pd(110) (44) except for the small features at ≈ 200 -270 K. After ion-bombardment and reactive oxygen cycles, no Au or other impurities are detected on the crystal face using AES. However, this desorption feature is always present even after extensive cleaning, and always with the same intensity. Following deposition of only 0.5 monolayers of Au, an intense, rather broad desorption feature centered at slightly lower temperatures, ≈ 225 K, is observed. We will refer to this feature as the α -state. When the Au coverage is increased to 1 monolayer, as in Fig.

Figure 3. A series of CO-desorption spectra from Pd(110) as a function of Au coverage
 Following Au deposition, the sample was exposed to 6L of CO, pre-annealed to 170 K, cooled to 130 K, prior to recording the desorption spectrum.

- a) Clean Pd(110)
- b) 1 Monolayer of Au on Pd(110)
- c) 2 Monolayers of Au on Pd(110)
- d) 3 monolayers of Au on Pd(110)

3(b), the high temperature features associated with the desorption of CO from clean Pd are completely suppressed. The α -state at 225 K is larger and is accompanied by a low temperature shoulder at ≈ 190 K. We will refer to the feature at 190 K as the β -state. With increasing Au coverage, Fig. 3(c,d), the β -state grows in intensity, and is accompanied by the simultaneous attenuation and loss of the α -state. These low temperature features are rather unexpected, but suggest some interesting interactions between the Au overlayer and the Pd substrate.

We have monitored the growth and suppression of these two desorption states with increasing Au coverage. The propagation of the α - and β -states with Au coverage, plotted as their respective peak heights at 225 K and 190 K, are displayed in Fig. 4. The Au coverage scale at the top of Fig. 4 is based on the minimum in the CO desorption yield of Fig. 2, which is taken as the completion of the first monolayer. Subsequent coverage values are based on evaporation times compared with that needed to complete the first monolayer. The peak height of the α -state displayed in Fig. 4 increases rapidly, and maximizes at a Au coverage of approximately 1-1.5 Au layers. It then falls to zero by slightly over 2 layers. Simultaneous with the maximum of the α -state yield, the β -state begins to populate. The β -state then maximizes at a coverage of 2 Au layers. When the Au coverage increases beyond 2 layers, the β -state peak height gradually decreases. As is evident, appreciable β -state intensity persists even for Au coverages in excess of 5 layers. These results will be further addressed in a latter section of this paper.

Figure 4. Plot of the CO-TDS peak heights for the α - and β -desorption states as a function of increasing Au coverage

C. LEED Measurements

The overlayer superstructures are followed as a function of film thickness and annealing temperature via a video-LEED system (43). The Au films are deposited by exposing the Pd crystal, held at the desired deposition temperature, to the Au vapor flux. The film thickness is determined using AES. After deposition and measurement of the Auger spectrum the sample is positioned in front of the LEED optics and the diffraction pattern is recorded. The crystal is then slowly heated to a desired temperature, held for 20 seconds at constant temperature to allow equilibration, and then quenched below 200 K where the LEED pattern is observed. The sequence is then repeated for the next annealing temperature. Diffraction spot profiles are recorded after each annealing cycle and processed with the video-LEED system (43).

We have measured the LEED intensity profiles as a function of Au coverage along the [001] (real space) direction between the (1,0) and (1,-1) beams. We have conducted experiments at substrate temperatures of 130 K and 300 K, and have found no difference in the resulting overlayer superstructures. All data presented follow deposition at a substrate temperature of 130 K. For a coverage of 1 Au monolayer a (1x1) diffraction pattern is observed, and no fractional order spots or streaking are detected. For Au coverages greater than 1 monolayer, we observe the appearance of additional fractional order beams that grow in intensity as the film is slowly annealed. These data are displayed in Fig. 5. At a coverage of 1.5 to 2.0 monolayers, Fig. 5(a) and 5(b) respectively, the Au films reconstruct irreversibly to a (1x2) at

Figure 5. LEED profiles for various Au coverages on Pd(110) as a function of annealing temperature

Profiles are taken along the [001] (real space) direction between the (1,0) and (1,-1) beams for a beam energy of 72 eV. Intensity scaling factors are given relative to that for the profile for the clean Pd substrate at 130 K.

- a) 1.5 monolayers of Au
- b) 2 monolayers of Au
- c) 3 monolayers of Au
- d) 4 monolayers of Au
- e) 5 monolayers of Au
- f) 6 monolayers of Au

temperatures slightly above 300 K. For the 1.5 monolayer film of Fig. 5(a), as the crystal is annealed to higher temperatures the half-order spots sharpen, and the best (1x2) is observed at 530 K. For temperatures over 530 K, the half-order spots are lost and a (1x1) pattern is recovered. For the 2 monolayer film of Fig. 5(b) the half-order spots are broader for lower temperatures, but sharpen and give a good (1x2) pattern at 640 K. As the temperature increases past 640 K the intensity of the half-order spots decrease and are finally lost after annealing to 770 K. When the Au coverage increases further to 3 and 4 monolayers, Fig. 5(c) and 5(d) respectively, the half-order spots split continuously and eventually a full (1x3) structure develops by 4 monolayers. The split half-order spots of Fig. 5(c) and 5(d) appear after annealing to slightly over 300 K, similar to the half-order spots of the lower coverage films. For both of these sets of data the fractional order spots sharpen and increase slightly in intensity as the temperature increases. For both the 3 and 4 monolayer profiles of Fig. 5(c,d), the split spots are lost after annealing to 640 K, leaving a (1x2) pattern. The (1x2) pattern remains, in both instances, up to an annealing temperature of 740 K. Only a (1x1) remains when these films are annealed to 770 K. For Au coverages in excess of 4 layers a (1x3) pattern is always observed after annealing, and follows the same evolution of superstructures with temperature as for the 3 and 4 monolayer cases. However, the quality of the diffraction pattern for these higher coverages degrades substantially. Shown in Fig. 5(e) and 5(f) are the profiles collected for Au coverages of 5 and 6 monolayers, respectively.

As is evident, the first order and fractional order beams decrease in intensity and broaden significantly. At these higher coverages the fractional order beams are scarcely visible above the background. The decrease in intensity in the spot profiles as coverage increases is depicted graphically in Fig. 6, where the intensity maximum (profile height) of the half-order component which develops into the $(1, -1/3)$ spot is shown as a function of Au coverage. By the time the half-order beam has split and the full one-third order position has been reached (4 monolayers) the intensity has decreased substantially. By a film thickness of 5 to 6 monolayers the intensity of the $(1, -1/3)$ spot relative to that for the 3 monolayer case has decreased by a factor of 10. For coverages of approximately 7 monolayers or greater, and for annealing temperatures of 640 K or higher where the (1×3) has transformed to the (1×2) , we also observe in addition to the attenuated and streaky (1×2) pattern very faint satellite spots which appear along the $[1\bar{1}0]$ (real space) direction for both the integral order and the fractional order beams.

The splitting of the half-order spot is an interesting observation. The degree of splitting does not change as a function of temperature, only as a function of coverage. The degree of splitting of the half-order spot for the data of Fig. 5 is shown in Fig. 7, where ΔK_1 is plotted vs. Au coverage for the component which develops into the $(1, -2/3)$ spot. The full third-order position, corresponding to $\Delta K_1 = 0.67$, is indicated by the horizontal dashed line of Fig. 7. At a film thickness of 2 layers only the half-order spot is present. At 4

Figure 6. The profile height of the fractional-order component which develops into the $(1, -1/3)$ spot plotted as function Au coverage in monolayers (ML).

Figure 7. Plot of ΔK_I for the fractional-order component which develops into the $(1, -2/3)$ spot vs. Au coverage in monolayers (ML)

monolayers, the spot has reached its full third-order position. For an intermediate coverage of 3 monolayers the spot is positioned half-way between the one half-order and third-order position. This indicates that the degree of splitting varies linearly with Au coverage.

The evolution of the LEED superstructures at higher annealing temperatures shows similarities to the high temperature phase transitions observed previously for the clean bulk surface of Au(110) (3,15-17). In these studies the (1x2) and (1x3) structures were found to interchange reversibly with the (1x1) structure when heated to temperatures between 650 and 900 K. The intensity profiles for the Au films at coverages of 1.5 to 2.0 layers, Fig. 5(a,b), show a transition from the (1x2) to the (1x1) at temperatures of 580 K and 770 K, respectively. However, unlike the clean surface transitions, the changes in the Au film morphology are irreversible. Similarly for coverages over 2 layers, Fig. 5(c,d), the split half-order beams revert first to a (1x2) structure at a temperature of 640 K, and then to a (1x1) structure at 770 K. The transitions for the films thicker than 2 monolayers are also irreversible. An explanation for the irreversibility of these structural transitions can be found in the AES data recorded for the films as a function of annealing temperature. These data are illustrated in Fig. 8, as the Au/Pd Auger ratio vs. temperature. It is clear that for temperatures in excess of 530 K, indicated by the vertical line of Fig. 8, the Au/Pd ratio for all the Au films has started to decrease. This decrease in the Au intensity is probably due to loss of the Au via dissolution of the overlayer into the Pd substrate. Au and Pd are known to form a

Figure 8. Variation of the $\text{Au}_{69}(\text{NVV})$ to $\text{Pd}_{330}(\text{MNN})$ Auger peak ratio versus annealing temperature for a series of Au coverages varying in thickness from 1.5 to 4 monolayers

continuous series of solid solutions over the entire composition range (62). The transitions for the films at high annealing temperatures are therefore not true thermodynamic phase transitions. Instead it is more probable that the transitions are a direct result of a decrease in film coverage as dissolution begins at the Au-Pd interface. The data, however, do not preclude the loss of Au as being due to agglomeration of the film rather than dissolution.

IV. DISCUSSION

A. Assignment of Low Temperature Desorption Features

During our initial investigation of the growth of Au films on Pd(110) we performed CO-TDS experiments to assist in Au coverage calibration. While carrying out these experiments we have observed some interesting results which seem to indicate a strong interaction between the first few Au overlayers and the Pd substrate. The low temperature desorption features which we refer to as the α -state (225 K) and the β -state (190 K) appear with the addition of Au ad-atoms as shown previously in Fig. 3. These features occur more than 100 K below the lowest CO desorption features associated with clean Pd(110) (44) and therefore we do not believe that they are associated with desorption from the Pd surface. It is possible that the Au atoms' electronic structure has been modified by the underlying Pd substrate and that these low temperature features can be attributed to desorption of CO from the Au overlayer. Support for the assignment of these low temperature features to desorption of CO from Au lies in the evolution of the α - and β -states with Au coverage.

The growth and decay of the α - and β -state, as shown in Fig. 4, follows a fascinating pattern. The maximum of the α -state yield at a nominal coverage of 1 layer, in addition to the subsequent maximum in the β -state and complete attenuation of the α -state at about 2 layers, brings about an interesting interpretation. These data suggest the possibility that the α -state is desorption of CO from the first layer Au atoms, and

that the β -state is the desorption of CO from second layer Au atoms. A schematic representation of adsorption sites, consistent with the observed desorption from the α - and β -states, is shown in Fig. 9 as a function of increasing Au coverage. As described previously, after deposition of 0.5 monolayers of Au the α -state appears. Concurrent with the appearance of the α -state at this Au coverage, the population of the CO desorption features occurring at temperatures over 300 K, which are associated with desorption from the Pd substrate, are attenuated by 50% (see Fig. 2). This attenuation is consistent with CO desorption from the unperturbed Pd sites which at 0.5 monolayers of Au should correspond to 50% of that of the clean Pd surface. This requires that the low temperature features at this coverage must be associated with the Au covered Pd surface. The schematic model for a 0.5 monolayer deposition is shown in Fig. 9(a). This picture illustrates the shielding of the Pd substrate by the Au ad-atoms resulting in attenuation of the high temperature features associated with direct desorption of CO from Pd, in addition to the creation of the adsorption sites associated with the first Au layer. It has been previously suggested by experimental (63) and theoretical results (64), that CO will adsorb mainly in a four-fold site on Pd(110), composed of 4 surface Pd atoms. We therefore place the CO molecules in our model in the same site. Due to the side view of the lattice of Fig. 9, the CO molecules are only shown as bonded to two of the four Pd atoms making up the four-fold site. Adsorption of CO in this first layer Au site is labeled α , corresponding to those CO molecules which would desorb in the α -state. As is evident from the schematic, CO

Figure 9. Schematic representation of CO adsorption sites as Au adatoms are deposited on Pd(110). The CO molecules labeled as α and β represent those molecules which would desorb in the α - and β -desorption states.

a) 0.5 Monolayers of Au
 b) 1 Monolayer of Au
 c) 2 Monolayers of Au
 d) 3 Monolayers of Au

molecules for the α state sit on a site directly over a Pd surface atom. When the first Au monolayer is completed only α -state CO molecules should be present, and at a maximum, as illustrated in Fig. 9(b). This picture is supported experimentally by the minimum in the CO desorption yield from Pd at a coverage of 1 monolayer (Au/Pd ratio of 0.4-0.5), shown in Fig. 2, and the maximum in the α -state at 1 monolayer as shown in Fig. 4. After addition of another 0.5 monolayers, the β -state desorption is now approximately equivalent to that in the α -state which indicates the coexistence of both first-layer and second-layer adsorption sites as modeled in Fig. 9(c). The CO molecules labeled as β in this picture correspond to those molecules which would desorb in the β -state. This picture is also consistent with the data of Fig. 4. As is evident from the model, CO molecules from the β state sit in a four-fold site directly over a first layer Au atom. When the second Au layer has been completed, the α -state should be completely suppressed and the β -state should be at a maximum. This is displayed schematically in Fig. 9(d), and also supported by the data of Fig. 4. When the Au coverage is increased beyond two monolayers, no additional desorption features which can be associated with desorption from the third or higher layers are evident. Only a gradual attenuation of the β -state is observed. Either the Au overlayers by this thickness have become almost bulk-like and have lost their ability to adsorb CO at these temperatures, or the desorption features associated with this layer are below 180 K, the minimum temperature at which desorption features can be observed due to our pre-annealing method described previously. We believe the previous

explanation is the more likely when compared to other experimental results for bulk-like chemisorption behavior on metal overlayers (65,66), although no experimental evidence is available to support this statement.

All the data presented strongly favor the assignments of the α - and β -states to desorption of CO from first and second layer Au sites, respectively. Although the assignments of these states as desorption of CO from Au layers seems logical from the experimental evidence provided, it would require that the Au have a rather strong interaction with the Pd substrate. It is known that CO does not adsorb on a bulk Au(110) surface even at temperatures as low as 125 K (60), which would require that a modification of the Au overlayer has occurred in order to adsorb CO at temperatures around 200 K. A previous study by Sachtler et al. (29) of Au monolayers on Pt(100) shows a similar increase in Au activity for monolayer quantities. In this study a pure bulk Au(100) surface was found to be inactive for the dehydrogenation reaction of cyclohexene to benzene where as the clean Pt(100) was found to catalyze the reaction. However, 1 monolayer of Au on Pt(100) enhanced the cyclohexene dehydrogenation rate by fivefold relative to the clean Pt(100). One of the explanations given by Sachtler et al. (29) for the enhanced reactivity was a possible electronic interaction between Pt and Au which might strongly affect the bonding of the hydrocarbons. This observation lends support to our hypothesis of Pd modified Au overlayers.

Changes in the CO chemisorption behavior for thin metal overlayers as compared to the overlayer metal in the bulk have been reported previously, for example, Pd on Au(111) (55,65), and Pd on Ta(110) (66).

In these studies an overlayer metal whose bulk surface strongly adsorbs CO is found to become more noble-metal like and shows signs of only weak CO chemisorption. This effect is explained by photoemission measurements (55,65,66) which indicate a reduction in the density of states near the Fermi level, apparently leading to weak chemisorption. Our observations for Au on Pd, however, indicate a strengthening of the CO bond. It is possible to rationalize our observations with a similar argument. That is, Au deposited on Pd has increased the density of states near the Fermi level which increases the Au-CO bond strength. This would account for the higher desorption temperatures for CO from Au found in our experiments. Evidence for changes occurring in the valence band for monolayers of Au on Pd(111) have been reported by Weissman-Wenocur *et al.* (32). For Au coverages between 0.3 and 1 monolayer a structure 4.2 eV below the Fermi level is observed with photoemission and does not appear to merge into the Au structure at high coverages. They tentatively assign this feature as a hybrid due to Pd-Au interactions. However, this feature probably lies too far below the Fermi level to influence the CO chemisorption behavior (65,67). But concurrent with the appearance of this hybrid state, the Pd derived structures at 0.4 and 1.5 eV below the Fermi level strengthen and sharpen relative to the clean Pd(111). This suggests a hybridization of the Au *sp* electrons with the Pd *d* electrons. However, Weissman-Wenocur *et al.* (32) argue that this explanation is unsatisfactory since a *spd* hybrid would tend to be less localized than a purely *d*-like electron and would therefore result in a broader rather than sharper structure. Although they could not offer a phenomenological

explanation for the enhancement of the structures near the Fermi level, it is direct evidence that the addition of Au, in the case of Pd(111), modifies this region of the valence band. We therefore believe that a similar phenomenon could be occurring in our Au on Pd(110) system. However, photoemission measurements similar to those for Au on Pd(111) (32) would need to be made before making any strong arguments. In any case, we take this as evidence that the modification of the Au overlayers by the underlying Pd(110) substrate is plausible, and consequently believe that our assignments of the α - and β -states as desorption of CO from the first and second Au layers, respectively, is correct.

As mentioned earlier, and as shown in Fig. 3(a), the CO desorption spectrum for clean Pd always shows a low temperature feature over the temperature range 225 to 270 K. It is interesting to note that in a previous study of Pd on Au(111) (55), after sputter cleaning of the surface the work-function for the clean Au could not be regained even though the Pd concentration had been reduced below the detection limit of AES. A chemical etch of the crystal surface was required to restore the work function to its original value. This was most likely due to dilute Pd which was present below the detection limit of AES. This type of phenomenon would help to explain the low temperature CO desorption peaks which are present even for the clean Pd substrate. These features could arise from desorption of CO from a Au/Pd alloy which may have formed on the surface or sides of the crystal. Au very likely is deposited on the sides of the crystal, but due to our normal incidence ion-gun it is not removed during ion-bombardment. This Au on the sides and/or Au below the

detection limit of AES which remains on the surface after sputtering, could alloy with the Pd as a result of high temperature anneals during cleaning cycles. Desorption of CO from an Au-Pd alloy, as opposed to desorption from Au on top of Pd would be expected to have a slightly higher desorption temperature. This would be consistent with our experimental observations for the low temperature peaks for the clean Pd (225 to 270 K) and those originating from the Au overlayers (≤ 225 K). If patches of an Au-Pd alloy do exist on the surface, they are definitely in the minority. We see no changes in the properties of the Pd crystal other than these low temperature CO desorption features. We are able to reproduce all the well known ordered LEED patterns for CO and H₂ on Pd(110) (68,69). If patches of a Au-Pd alloy do exist, we believe they would be too small to have any measurable effect on any of our conclusions presented here.

B. Identification of Growth Mode

Although the experimental data agree well with a layer-by-layer growth mechanism, some indications of imperfect growth are evident. The appearance of the β -state at a coverage of 1 Au layer, Fig. 3, would seem to suggest some contributions from second layer Au atoms before completion of the first layer. In addition, the existence of the α -state for coverages slightly over 2 layers indicates partial filling of the third layer before completion of the second. This trend towards three dimensional growth as the coverage is increased is further supported by the gradual decrease in the β -state peak height occurring for coverages

in excess of 2 monolayers as shown in Fig. 4. Growth in this manner would be consistent with some availability of second layer sites even for coverages in excess of 3 layers. This scenario is portrayed in Fig. 9(e). These data imply that for Au deposited on Pd(110) at 130 K, the films tend to grow layer-by-layer for the first two layers with some degree of imperfection, with films greater than two layers growing more three-dimensionally. Thus the data are most consistent with a Stranski-Krastanov growth mode (52), with a critical coverage of 2 layers.

The small degree of imperfection perceived for the growth of the first two layers is probably due to reduced ad-atom mobility during deposition at 130 K, which inhibits perfect layer-by-layer growth. However, in light of a recent report by Fenter and Gustafsson (40) the imperfection for these first two layers could have an alternative explanation. Using medium-energy ion scattering they report a growth mechanism for the Au on Ag(110) system in which Au grows epitaxial on the Ag in a "bilayer" form at room temperature. That is, they find for a deposition of 1 monolayer of Au that half of the surface is covered by Au "bilayers", presumably in islands. For coverages in excess of 1 monolayer the Au is found to grow in a "bilayer" Volmer-Weber growth mode (three-dimensional islanding before covering of the substrate) (52). It is possible that the tendency towards imperfection in our Au on Pd(110) system is driven partially by this "bilayer" mode found for Au on Ag(110) (40). However, we do not believe that our system follows a complete "bilayer" mechanism as that for Au on Ag(110). Our CO-TDS results do indicate small contributions from second layer Au atoms before completion

of the first as evidenced by a coexistence of the α - and β -states for 1 monolayer of Au, Fig. 3(b). However, at this coverage the CO desorption yield from unperturbed Pd has already reached a minimum, Fig. 2, indicating that all Pd sites are covered by Au atoms. If the minimum in the CO desorption yield from Pd was due to the completion of a perfect "bilayer" instead of a single monolayer, one would expect an Auger ratio higher than 0.5, the point of complete attenuation of Pd-CO desorption, for the "bilayer". We showed earlier that for layer-by-layer growth a monolayer of Au on Pd should result in an $Au_{69}(NVV)$ to $Pd_{330}(MNN)$ Auger ratio of 0.5, and two monolayers, or a "bilayer", should produce an Auger ratio close to 1.0. For a "bilayer" to correspond to an Au/Pd ratio of 0.5 would require an error of 120% in these calculations. A possible source of error for these calculations is the inelastic mean-free-paths. However, to reduce the Au/Pd Auger ratio by 50% would require an increase in the inelastic mean-free-paths from 4 to 8 Å for the $Au_{69}(NVV)$ and from 7 to 14 Å for $Pd_{330}(MNN)$. We do not believe that this would be reasonable. An error could also be created by our assumption of layer-by-layer growth. However, if Au on Pd(110) followed a "bilayer" Volmer-Weber growth mode, the coverage at which the Pd would be completely covered would be much greater than 2 monolayers, and one would expect a Au/Pd Auger ratio larger than 1:1 not 50% less. For the Au on Ag system a Volmer-Weber growth mode (52) is expected in light of the surface free energies, 1.63 J/m² for Au and 1.30 J/m² for Ag (70,71), which may increase the tendency toward "bilayer" growth. For Au on Pd however, layer-by-layer growth is expected. The surface free energy of Au is 1.63

J/m^2 while that for Pd is 2.04 J/m^2 (70,71). Therefore the thermodynamics for the Au-Pd system would tend to disfavor growth as bilayers. We therefore believe that a Stranski-Krastanov mode (layer growth followed by clustering) (52) best describes the growth of Au on Pd(110) at 130 K, the slight degree of imperfection for the first two layers being due to kinetic limitations of the growing film. This assignment is consistent with the mode of growth found for Au on Pd(111) at room temperature (33-35), where layer growth also breaks down for coverages in excess of 2 layers due to an increasing strain energy resulting from the 4.8% lattice mismatch for the Au-Pd system. However, a slight tendency toward "bilayer" growth can not be completely ruled out in our case. A complete study using a technique which is more sensitive to the three-dimensional structure of the film would be necessary to resolve this uncertainty.

C. Origins of (1x2) and (1x3)

While monitoring the LEED patterns of Au overlayers as a function of coverage and temperature we have observed both (1x2) and (1x3) superstructures. In light of our observation of the dissolution of Au into the Pd substrate at temperatures close to that at which we observe the sharpest LEED patterns, Fig. 5 and 8, and the assumed alloying in our CO-TDS as discussed in section IV(A), there is a question as to the origin of the (1x2) and (1x3) structures. That is, are they due to true surface reconstructions, or are they due to the formation of an ordered alloy. Both (1x2) and (1x3) reconstructions have been reported

previously for the clean bulk surface of Au(110) (3,7,15-21,24,25,27). Although no reports of ordered surface alloys for the Au-Pd system have been reported, the bulk phase diagram for the Au-Pd system does indicate evidence of Au-Pd bulk ordered alloys (62). However, while working with overlayers of Pt on Pd(110) we have observed the formation of the same (1x2) and (1x3) structures (72). For the Pt/Pd system we can test for a true surface reconstruction through the adsorption of CO, since CO is known to "lift" the (1x2) and (1x3) surface reconstructions returning the surface to a (1x1) structure (6,13). Indeed the (1x2) and (1x3) structures for Pt on Pd(110) are found to be completely reversible with the (1x1) upon the adsorption and desorption of CO demonstrating that they are true surface reconstructions. Although we do not have a means available to test the Au superstructures, we believe that the similarity between (1x2) and (1x3) structures for both Au and Pt on Pd(110), and the fact that bulk Au(110) is known to show both the (1x2) and (1x3) patterns, is sufficient evidence to qualify the Au superstructures as true surface reconstructions.

To begin our discussion of the reconstructions of the Au overlayers we shall start with a basic review of the reconstruction of the (110) surface. The (1x2) and (1x3) reconstructions fall into the category referred to as "missing row" reconstructions. That is, in the case of the (1x2) every other row along the [001] direction is missing. This change in periodicity from the unreconstructed (1x1)-(110) surface to the (1x2) and the (1x3) surfaces is displayed in Fig. 10. The model for the (1x2) "missing row" reconstruction, Fig. 10(b), is quite well accepted.

Figure 10. Schematic representation of the (110) unreconstructed and reconstructed surface

- a) Unreconstructed (1x1)
- b) Reconstructed (1x2)
- c) Reconstructed (1x3)

Reconstructions of this type have been studied extensively, e.g., Au (3,7,18-21,23,25), Pt (5,9-13,22,23) and Ir (2,14) and most seem to favor the "missing row" structure. The (1x3) reconstruction, although observed less frequently, is also thought to fall into the category of a "missing row" structure (3,7,9). A model for the (1x3) is shown in Fig. 10(c). In contrast to the reconstruction of the more atomically smooth (111) and (100) surfaces the reconstruction of the (110) surface involves a transition to a micro-faceted surface resulting in the formation of (111) micro-facets along the trough walls (Z). The difference between the (1x2) and (1x3) lies in the degree of faceting for these two structures. This faceting involves removal of first layer atoms for the (1x2) reconstruction, and both first and second layer atoms in the case of the (1x3) reconstruction, as displayed in Fig. 10(b) and (c), respectively. It seems intuitively obvious that in the case of the reconstruction of thin films on the (110) substrate there would be a coverage dependence involved with the degree of faceting.

We do indeed observe a coverage dependence for the reconstruction of the Au films on Pd(110). For films of 1 monolayer or below we only observe a (1x1) diffraction pattern over the entire temperature range studied. As coverage increases additional fractional order beams develop as the films are annealed. Recall from Fig. 5(a) and (b) the development of a (1x2) superstructure for films of 1.5 and 2 monolayers respectively. As the coverage increases further, Fig. 5(c) and (d), the half-order spots split continuously and finally a full (1x3) structure develops by 4 monolayers. The evolution of these superstructures directly depends on

the thickness of the deposited overlayer.

Previous studies of the reconstruction of metal films have focussed on the thickness of the overlayer required to support a bulk-like reconstruction. For Au on Pt(100) (30) and Au on Pd(100) (28), three to four layers must be present before bulk-like reconstructions can take place. However, for Pt on Pd(100) (37) only a single monolayer of Pt is necessary to support the (5x1) reconstruction. No reconstructions of films of Au, Pt, or Ir on (110) surfaces have been reported to this date. Fenter and Gustafsson who studied Au on Ag(110) at room temperature (40) did not observe any evidence of reconstruction for their overlayers. Therefore no information for the dependence of reconstruction on overlayer thickness for films on a (110) substrate is available for comparison. However, due to the faceted nature of the (1x2) and (1x3) "missing row" type of reconstruction we can project some minimum thicknesses required to support such a transformation for the Au on Pd(110) system.

Let us start with the (1x2) reconstruction, and remember that our substrate is stable against reconstruction (41,42) and therefore we consider it only as a passive template for growth, i.e., it does not participate in the reconstruction. For the case of a single monolayer of Au on Pd(110) it seems unlikely that reconstruction could occur at this low coverage. This would require the removal of Au atoms which are in direct contact with the Pd surface. This can be seen visually in Fig. 10 (a) and (c) if we assume the first layer atoms (open circles) represent the Au monolayer and the under-lying atoms represent the Pd substrate.

The transition from the (1x1), Fig. 10(a), to the (1x2), Fig. 10(b), requires the removal of every other row of Au atoms which are in direct contact with the Pd substrate. It is also hard to conceive how the electronic structure of a single monolayer on a open surface structure such as the (110) could mimic that of the bulk. In addition, in light of our experimental observation of a strong interaction between the first Au layer and the Pd substrate it seems improbable that first layer Au atoms could be easily removed. However, by a thickness of two layers the electronic structure of the bulk is usually approached (65,66), and now the reconstruction would only require removal of Au atoms in direct contact with first layer Au atoms. A reconstruction under these conditions would seem more feasible. Therefore we believe that a minimum thickness of 2 monolayers of Au would be necessary to support a (1x2) reconstruction. In the case of a (1x3) reconstruction, both first and second layer atoms need to be removed (see Fig. 10(c)). For reasons given previously this type of reconstruction should be impossible for a depth of only one Au layer, and improbable for a thickness of two layers due to the requirement of the removal of Au atoms in direct contact with the Pd substrate as we have argued against previously. We do not feel that a (1x3) structure is possible at a coverage of only 1 to 2 monolayers. However, by a film thickness of 3 Au layers and for reasons similar to those given for the (1x2), the (1x3) should be attainable. Therefore we believe a minimum depth of 2 layers for the (1x2) and 3 layers for the (1x3) should be necessary to support these reconstructions.

Referring back to Fig. 5, in which we present LEED profiles for Au films as a function of overlayer thickness and temperature, we observe (1x2) and (1x3) superstructures at coverages close to those proposed for the minimum coverages required to support these reconstructions. For a Au coverage of 1 layer or below, no changes in the LEED pattern are observed other than a slight attenuation of the substrate (1x1) pattern. For coverages between 1.5 and 2 layers, Fig. 5(a) and (b) respectively, a (1x2) pattern develops upon annealing. Although we proposed that a thickness of 2 layers should be the minimum required to support a (1x2) we can see this pattern already for the 1.5 monolayer film. The observation of the (1x2) at a coverage of only 1.5 monolayers is just a result of the contributions to the diffraction pattern from those areas of the film which are 2 layers thick. At this coverage approximately 50% of the second layer should be filled and it is thus possible for reconstruction to occur for these bilayer areas. A more intense (1x2) pattern which is stable to higher temperatures is observed for the 2 monolayer Au film, Fig. 5(b). The higher intensity, and possibly the increased thermal stability of the (1x2) for 2 layers is the result of a higher density of reconstructed film, which should be at a maximum at 2 complete layers. For coverages greater than 2 layers the half-order spots split continuously and by a coverage of 4 monolayers a complete (1x3) is formed. The development and maximizing of the (1x2) at a film thickness of 2 layers of Au is easy to interpret, although the evolution of the (1x3) by the continuous splitting of the half-order spots as coverage is increased is more perplexing.

D. Explanation for Spot Splitting

The splitting of the half-order spot as the (1×3) structure develops is another interesting observation for this system. To the best of our knowledge, no similar observations have been reported for reconstructions of bulk fcc (110) surfaces or for the reconstructions of metal films. However, similar observations have been reported for several lattice gas systems (73-75). Here we shall concentrate on a comparison with the work by Ertl and Kuppers for O/Pd(110) (76,77), for which a more complete explanation has been developed. The O/Pd(110) system is one in which the interactions between adsorbed particles is anisotropic. That is, attractive interactions exist along the $[1\bar{1}0]$ direction while repulsive interactions exist between nearest and next-nearest neighbors in the $[001]$ direction. Monte-Carlo simulations for the equilibrium configuration of adsorbed O atoms have been completed (76,77) and have been shown to result in parallel rows of O atoms along $[1\bar{1}0]$ direction with a more or less uniform distribution of spacings $2a$ and $3a$ in the $[001]$ direction. The spacing (a) represents the trough repeat distance in the $[001]$ direction for the Pd(110) substrate. In addition to the computer simulations, beam profiles constructed from the equilibrium simulations as a function of O coverage are also given (76,77). The form these profiles take, as the O coverage changes, show a marked resemblance to the profiles we have obtained for Au on Pd(110) as the Au coverage is varied. The profiles show maxima at third-order positions for $\theta=0.33$ which continuously move together to a half-order spot at $\theta=0.50$. This results from a transition in the distribution of O chains of distance $3a$

to that of only 2a as the O coverage increases and fills up the empty rows. The observed splitting then is a result of a coexistence of these two distributions of adsorbed O atoms. As mentioned previously, similar observations have been reported by Germer et al. for O on Ni(110) (74). They also concluded that the splitting was due to a mixture of the two phases arranged in a similar manner. Although this work involves the structure of metal overlayers and not a lattice gas system a similar explanation can be given for our results.

Our profiles for overlayers of Au on Pd(110) show a transition from that of a half-order spot continuously splitting into third order spots as the Au coverage is increased, Fig. 5. We know that the (1x2) is due to a missing row reconstruction and maximizes when the Au overlayer thickness reaches two layers. We have previously speculated that the minimum coverage required to support a (1x3) missing row reconstruction for this system would be 3 monolayers. As the Au coverage increases past 2 monolayers (but less than 3 monolayers) there will exist regions of the film that are both two and three layers deep. It is therefore possible that upon annealing and reconstruction of the film, regions of (1x2) and (1x3) coexist and result in the spot splitting. As the coverage increases the density of the (1x3) regions increases relative to the (1x2) regions, and thus the spots diverge into third-order spots. The reason for the incomplete formation of the (1x3) at a coverage of 3 monolayers must be a result of the three-dimensional growth for coverages greater than 2 layers, which results in a coexistence of (1x2) and (1x3) phases even for these higher coverages. The effect of three-dimensional

growth is already evident at 2 monolayers where the half order spot has started to broaden but has not noticeably split, Fig. 5(b). We believe that this is a reasonable explanation for the observed spot splitting.

The spot splitting for this system must be due to a rather random distribution of small (1x2) and (1x3) regions, similar to that found for the equilibrium distribution of adsorbed O on Pd(110) (76,77). Individual areas of these reconstructed regions must be less than the coherence length of the LEED optics, typically 50-100 Å (78), or we would observe a super-position of the (1x2) and (1x3) diffraction patterns instead of the half-order spot splitting. In order for the distribution of (1x2) and (1x3) regions to be rather random, this would require that the third layer Au ad-atoms also be rather well dispersed, or possibly in small well dispersed islands or clusters. Clustering for coverages in excess of two monolayers is suggested by our CO-TDS measurements as discussed previously in section IV(B).

E. Formation of (1x2) vs (1x3)

The existence of both (1x2) and (1x3) structures found in this study raises the question as to which represents the most stable configuration for the clean Au surface. As stated previously, both of these structures have been observed experimentally (3,7,15-21,24,25,27). However, the (1x2) has been reported most frequently. For the Au on Pd(110) system, we initially thought that the (1x3) structure is most likely induced by an electronic interaction between the Au and Pd and would thus revert back to the (1x2) at higher coverages. However, for coverages as high as

7 layers we still observe third-order spots, although they are very faint and streaky. This evidence would suggest that the (1×3) is the more stable of the two. If this is indeed true, why isn't the (1×3) observed most frequently for the clean Au(110) surface? Because of this puzzling question we have looked for an alternative explanation for the (1×3) .

Our explanation revolves around a previous statement, in which we concluded that the spot splitting for this system must be due to a rather random distribution of small (1×2) and (1×3) regions. This statement insinuates small uniformly mixed domains of the (1×2) and (1×3) phases, which in turn suggests the presence of domain boundaries. If we look at the pure (1×2) phase, the periodicity repeats every second lattice spacing. This periodicity provides the opportunity for the existence of antiphase domains. That is, (1×2) domains are displaced by one lattice spacing along the $[001]$ direction. If we look at a structural model of an antiphase domain boundary for a pure (1×2) phase, we find that the boundary results in the formation of a (1×3) channel. This formation of a (1×3) channel at the antiphase domain boundary of a pure (1×2) phase is represented schematically in Fig. 11. In this picture a pure (1×2) phase is shown in Fig. 11(a), and the formation of an antiphase domain is represented in Fig. 11(b). We can see that the (1×2) phase at the left side of the lattice model of Fig. 11(b) is out of phase with the (1×2) phase on the right side of the lattice model by a single lattice spacing. At the domain boundary, two consecutive rows are missing resulting from the continuation of the "missing row" arrangement for each respective domain. The displacement of these consecutive rows results in the

Figure 11. Schematic representation of the formation of a (1x3) channel at an antiphase domain between two (1x2) phases

formation of a (1x3) channel at the domain boundary as is evident in Fig. 11(b). A (1x3) channel such as that described in Fig. 11(b) has been observed experimentally in a scanning tunneling microscope (STM) study by Binnig *et al.* (7) for the clean Au(110) surface. In this study they report the existence of (1x2), (1x3), and even (1x4) channels in areas exhibiting strong disorder. An STM picture of a disordered region, Fig. 2 of Ref. (7), clearly shows a (1x3) channel forming at a boundary between two (1x2) channels which are out of phase by one lattice spacing. The existence of antiphase domains could explain the development of the (1x3) phase. This would suggest that the (1x2) is truly the more stable phase and the formation of the (1x3) phase for bulk Au possibly depends on sample preparation conditions, i.e., heating and cooling rates, or for our case the growth characteristics of the film.

With the above argument in mind, how then, if the (1x3) forms only at antiphase domains, can this explain our initial conclusion of a rather random distribution of small (1x2) and (1x3) regions? Remember that for 2 monolayers of Au, we only observe the (1x2) structure. However, as Au coverage increases, the half-order spot splits and the full (1x3) develops by 4 monolayers. Evidently for the 2 monolayer case the (1x3) channels don't form, or are not frequent enough to cause splitting of the half-order spots. At 2 monolayers the film thickness may be too thin to support such a channel and therefore they do not form. This coverage dependence was speculated upon previously in section IV(C). However, the other possibility is that the (1x3) channels form but the (1x2) domains are so large that they don't contribute significantly to the diffraction

pattern. As is evident in Fig. 5(b) the half-order spots are broad but are not split. This broadening is only observed along the [001] direction, i.e., across the channels. This does, however, indicate some degree of disorder for this coverage of Au. The existence of larger (1x2) domains for the Au film of 2 monolayers may be substantiated by the more two dimensional nature of the film at this coverage. Recall that we concluded earlier that the film grows layer-by-layer for the first two layers and then appear to grow more three-dimensionally as coverage increases. This trend toward three-dimensional growth may help to explain the formation of a higher density of antiphase domains as the coverage exceeds 2 monolayers, and thus the coexistence of (1x2) and (1x3) regions.

Envision a perfect two-dimensional (1x1) surface of Au(110), as shown in Fig 10(a). As temperature increases and reconstruction (or reordering of the surface) begins, it is assumed that a perfect (1x2) will result as shown in Fig. 10(b). However, we know that no system is ideal, and there will exist disruptions in the long range order. These disruptions can result, for example, from the presence of atomic steps or defects. The presence of these disruptions can cause ordering to start at a large number of nucleation sites, possibly shifted by odd integers of the lattice spacing, thus giving rise to the existence of antiphase domains. For our system of Au on Pd(110), as the coverage increases beyond 2 monolayers, the film begins to grow more three-dimensionally. That is, the vertical propagation of the film increases relative to that for the horizontal direction. This also can be envisioned as a

disruption in the long range two-dimensional morphological order of the system. This disruption may result in the localization of the ordered (1x2) phase over a very short distance and would thus increase the probability for the formation of antiphase domains and thus (1x3) channels. As coverage increases and the trend toward three dimensional growth increases, the degree of disruption in the long range order (smoothness) should also increase proportionally. Therefore at some point the (1x3) channels from the antiphase domains may become the majority species. This would be consistent with our observation of the development of the full (1x3) diffraction pattern at 4 monolayers. Further evidence for an increase in two-dimensional disorder for coverages exceeding 2 monolayers is evident in Fig. 6, which shows the continuous decrease in the fractional-order spot profile intensity as coverage increases. By a coverage of 6 monolayers the diffraction pattern is very streaky, and the fractional-order beams are barely distinguishable above the background. It is most likely that the three-dimensional nature of the growing film is the principal cause for the deterioration of the diffraction pattern at higher coverages.

The conclusion which we can draw from the above arguments is that the (1x2) appears to be the predominant structure for the clean Au(110). The few reports for the observation of the (1x3) for the case of bulk Au (3,7,15) may be due to differing sample preparation procedures resulting in varying degrees of two-dimensional order. The transition to the (1x3) for our Au films probably results from an increase in the amount of disorder of the system resulting from the trend toward three-dimensional

growth. These disruptions in the order lead to an increased density of antiphase domains for the (1x2) phase which eventually results in the dominance of the (1x3) structure. As mentioned previously the coexistence of these two phases must be rather random and well mixed suggesting very small domain sizes. Our experimental results do not give us an idea of the actual domain size of the two phases present. However, a publication by Houston and Park (79) in which they make calculations for continuous beam splitting during the transformation from a double-spaced to a triple-spaced structure gives us some insight to this question. Their calculations provide values for the average domain length, given in units of the substrate lattice spacing, corresponding to a certain degree of splitting for the half-order spot. Comparing Houston and Park's results (79) with the degree of splitting for our 3 and 4 monolayer films shown in Fig. 7, gives us a value for the average domain length of only 6 lattice spacings for the 3 monolayer case and 3 lattice spacings for the 4 monolayer case. That is by the time the third-order component of the split half-order beam has reached its full third-order position the average domain length is on the order of only a few lattice spacings. This comparison then gives us some indication of the average degree of disorder resulting from the three dimensional growth of the film.

V. CONCLUSIONS

We have presented the results of an in depth study of the growth and reconstruction of Au films grown on Pd(110). Following deposition of the first two monolayers of Au, we observe some interesting low temperature CO desorption features which we attribute to desorption of CO from the Au overlayers. This is the first observation of CO adsorption on Au at temperatures over 125 K, which suggests that the Au overlayers, at least the first two layers, are modified by the underlying Pd substrate. These CO-TDS experiments also yield information which assists in characterization of the growth mode for Au on Pd(110). Our experimental data is most consistent with Stranski-Krastanov growth mechanism (52) in which the Au grows layer-by-layer for the first two layers and then grows more three-dimensionally for higher coverages. A similar conclusion was reached for the growth of Au on Pd(111) (33-35), and presumably occurs due to an increase in lattice strain as coverage increases, resulting from the 4.8% lattice mismatch for this system.

The fact that we observe the low temperature CO desorption suggests that the Pd in some way influences the electronic structure of the Au. We do not believe that at the temperature at which we deposit, 130 K, or at the temperatures at which we see these low temperature features, 190 and 225 K, any mixing of Au and Pd occurs. We have no data to substantiate this statement, although previous work for Au on Pd(111) using ion scattering (34) found no evidence of interfacial mixing at room temperature. In addition, we believe that the (1x2) and (1x3)

superstructures are true "missing row" reconstructions and not due to the formation of an ordered alloy. The superstructures resemble those which have been reported previously for the clean Au(110) surface (3,7,15-21,24,25,27) and in addition we have observed the same structures for Pt films on Pd(110) (72) which we have proven to be true reconstructions of the Pt films.

During LEED experiments of the Au overlayers we find the (1x2) and (1x3) superstructures to depend on the Au overlayer thickness. We believe that both of these structures pertain to "missing row" type reconstructions. However, to be more conclusive we are presently collecting I-V spectra for these structures for both the Au and Pt films in hopes of obtaining more concrete evidence to support this conclusion. The I-V calculations are to be performed by M. Lindroos at Tampere University of Technology in Tampere, Finland. An interesting result found for these structures is that the (1x3) evolves from the (1x2) by the continuous splitting of the half-order spot as the Au coverage is increased. We explain this phenomenon as being due to the coexistence of random (1x2) and (1x3) regions, each being smaller than the coherence length of the LEED optics, which results in the splitting. We believe that the (1x2) structure is the true stable structure for the clean Au(110) surface. The transition to the (1x3) is not due to an electronic perturbation from the Pd substrate, but instead can be attributed to the formation of antiphase domains for the (1x2) phase which result in the formation of (1x3) channels. As the Au coverage increases past 2 monolayers a transition to three-dimensional growth occurs, resulting in

a disruption in the long range order (smoothness) of the film and thus the formation of antiphase domains. As coverage increases so should the degree of disorder, and therefore at some point (in our case a coverage of 4 monolayers) the density of (1x3) channels from the antiphase domains may become the majority species. This then gives rise to a (1x3) diffraction pattern. The (1x3) phase reported by other researchers for bulk Au (3,7,15) may result from varying sample preparation procedures.

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PAPER III:

Pt FILMS ON Pd(110): DEPENDENCE OF (1X2) AND (1X3) RECONSTRUCTIONS
ON FILM THICKNESS AND DEPOSITION TEMPERATURE

Pt FILMS ON Pd(110): DEPENDENCE OF (1X2) AND (1X3) RECONSTRUCTIONS
ON FILM THICKNESS AND DEPOSITION TEMPERATURE

P. J. Schmitz, H. C. Kang, W. -Y. Leung, and P. A. Thiel

Department of Chemistry and Ames Laboratory
Iowa State University
Ames, Iowa 50011

ABSTRACT

We present the results of a study of the structure of Pt films grown on Pd(110) at adsorption temperatures of 130-300 K, and annealed at temperatures up to 800 K. We observe (1x2) and (1x3) reconstructions, depending upon the Pt coverage and deposition temperature. The (1x2) develops upon annealing to ca. 410 K, only if the film is 3 monolayers and is deposited between 130 and 200 K. If the same amount of Pt is deposited at higher substrate temperatures, a (1x3) develops upon annealing. At all higher Pt coverages, annealing brings on the (1x3) structure, independent of the deposition conditions. Adsorption of CO "lifts" both the (1x2) and (1x3) Pt film structures, confirming that both are reconstructions. This is the first observation that reconstruction in a film can depend upon the conditions of its deposition.

I. INTRODUCTION

The growth and structure of ultra-thin metal films (1 to 10 monolayer regime) is an on going topic of research in our laboratories (1-4). We have been particularly interested in the growth of metal films whose bulk surfaces are known to reconstruct (1,4), and how the factors which control film growth can affect the bulk-like reconstructions of these films. The (100) and (110) low index faces of bulk Au, Pt, and Ir are known to reconstruct, i.e., their surfaces rearrange to form an atomically different two-dimensional periodicity than that of the bulk crystal (5, and Ref. therein). Since the rearrangements in these systems are known to be limited to the first few atomic layers (5), the study of thin films of these metals provides a unique way of determining how and under what conditions these metals may exhibit their bulk-like reconstructions. Many studies of the growth of Au and Pt overlayers have appeared in the literature (1,6-15). However, all workers to date, except Fenter and Gustafsson (16), have studied the growth of these metals on the more atomically-smooth fcc (111) and (100) crystal faces. We therefore have recently concentrated our efforts on the study of metal films on an fcc (110) substrate, Pd(110). The clean (110) surface of bulk Pd is stable against reconstruction (17,18).

The (110) faces of Au, Pt, and Ir are known to exhibit (1xn) "missing row" reconstructions, where n can take the values of 2,3, and even higher integers (5,19-39). We have recently reported results on the growth and reconstructions of Au films on Pd(110) (4). For this system

we find evidence for both (1x2) and (1x3) reconstructions, their formation depending upon film thickness. We believe that the (1x2) to the (1x3) transition observed in this system is a direct result of the three-dimensional growth of the film resulting from the strain induced by the 4.8% lattice mismatch. We have therefore directed our efforts to the growth of Pt films on Pd(110) for purposes of comparison. As mentioned previously bulk Pt also exhibits similar "missing row" reconstructions. However, Pt and Pd have a very small lattice mismatch, 0.8%. By studying the growth of Au and Pt films we therefore have a means of comparing how the differing growth conditions can effect the bulk-like reconstructions for these systems.

II. EXPERIMENTAL PROCEDURES

The experiments are carried out in an ultrahigh vacuum chamber equipped with a shuttered Pt evaporation source, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), optics for low-energy electron diffraction (LEED), and provisions for controlled gas exposure. Base pressures are below 2×10^{-10} Torr. The LEED patterns are monitored with a video imaging system as described previously (40).

The Pd crystal which has been oriented to within $\pm 1^\circ$ of the (110) plane is the same as that used previously (4). The crystal is cleaned by repeated cycles of argon-ion bombardment (1 keV, $1.5 \mu\text{A}/\text{cm}^2$) at 300 K, followed by cycling in oxygen to remove carbon and heating to 1100 K to desorb residual oxygen. The surface cleanliness is determined by AES, and by CO thermal desorption which gives spectra equivalent to those reported previously for a carbon free surface (41). The sample is mounted by spotwelds to two Ta support rods which in turn are connected via copper braids to current feedthroughs in a liquid nitrogen reservoir. This configuration allows the sample temperature to be varied from 130 K up to 1100 K by resistive heating of the crystal. The crystal temperature is monitored by a W-5% Re/W-26% Re thermocouple spotwelded to the back of the sample. The temperature is controlled through a feedback circuit designed by Herz *et al.* (42).

Pt is deposited on the sample surface from a resistively-heated tungsten filament wrapped with 0.25mm diameter Pt wire (99.95%), following the design of DeCooman and Vook (43). The Pt source is

enclosed in a double-walled, liquid-nitrogen-cooled shroud with a 1.5 cm orifice to allow Pt vapor to escape toward the sample. Evaporation rates are on the order of one monolayer per minute. After thorough outgassing of the filament, a pressure rise of $\sim 4 \times 10^{-10}$ Torr above the background (2×10^{-10} Torr) was observed during a typical 60 second evaporation. No impurities can be detected by AES after deposition of the films. Also using AES, the Pt distribution across the sample surface is found to be uniform to within $\pm 5\%$. The Pt is removed by argon-ion bombardment after each experiment. The conditions of bombardment are 1 keV, ca. $1.5 \mu\text{A}/\text{cm}^2$, at 300 K.

The Pt films are deposited by exposing the Pd crystal, held at the desired deposition temperature, to the Pt vapor flux. The resultant film thickness is determined by AES. After deposition, the sample is slowly heated to a desired temperature, held for 20 seconds at constant temperature, and then quenched below 200 K where the LEED pattern is observed. The sequence is then repeated for the next annealing temperature. Diffraction spot profiles are recorded and processed with the video-LEED system (40).

III. EXPERIMENTAL RESULTS

We present the results of a study of the growth and reconstruction of Pt films on Pd(110) using AES and LEED. AES is used to determine the Pt film thickness, and also to follow the Pt concentration at the surface relative to Pd as the system is annealed to higher temperatures. LEED is used as a means of following the evolution of the two-dimensional surface structure of the Pt films as temperature is increased. We have also completed simple adsorption-desorption experiments using CO as a means of comparing the response of the Pt film structure to an adsorbate with the response of the bulk Pt(110) surface. Experiments using H₂ are also conducted to rule out H surface contamination as a contributing factor in our results.

A. Coverage Calibration

We rely primarily on AES as a means of calibrating our film thicknesses. As has been shown previously (e.g., 44-46), if a metal film grows in a layer-by-layer fashion (Frank-van der Merwe mode) the attenuation of the substrate and growth of the overlayer Auger signals can be used as a means of calibrating the first and subsequent monolayers. This is possible because the second metal layer less effectively attenuates the substrate Auger signal than the first, and if the substrate and overlayer Auger intensities, or the ratio of the overlayer and substrate Auger intensities (47) are plotted vs. deposition time, a discontinuity in slope will appear at the point the second layer

begins to populate. This method of looking for discontinuities in slope has been a popular means of calibrating metal film thickness.

Our initial investigations involved monitoring the Pt films using AES to determine the coverage and the growth mode. We therefore begin by monitoring the $Pt_{64}(NVV)$ and $Pd_{330}(MNN)$ Auger intensities as a function of deposition time for deposition at 300 K. The results of these measurements are shown in Fig. 1 where the peak-to-peak amplitudes and the ratio of the peak-to-peak amplitudes of the $Pt_{64}(NVV)$ and $Pd_{330}(MNN)$ derivative spectra are plotted as a function of deposition time. We have drawn straight line segments through the data of Fig. 1(a) and Fig. 1(b) to accentuate the points where slight breaks in the slope occur. These discontinuities are found for deposition times of 55 and 100 seconds, corresponding to Pt/Pd intensity ratios of 0.4 and 0.8, respectively. Similar to our work with Au on Pd (4), these breaks are very subtle, and the assignments are somewhat subjective. The absence of clear delineating segments in the AES data do not rule out layer-by-layer growth (1,2). However, it does make coverage calibration rather difficult if a complementary method for calibration is not available.

Past research in our laboratories has shown the utility of standard LEED optics as a means of calibrating metal film growth by monitoring the progression of Bragg intensity oscillations with deposition time (2,48). However, this technique has not been useful in our study of Au on Pd(110) (4) or in our present study of Pt films presumably due to the existence of a minimum in the I-V curve at the out-of-phase condition. In our Au on Pd(110) study (4) we used CO thermal

Figure 1. Variation of the Pt₆₄(NVV) to Pd₃₃₀(MNN) Auger signals versus deposition time following deposition at 300K
 a) Plotted as the peak-to-peak amplitudes of the Pt and Pd derivative spectra.
 b) Plotted as the ratio of the peak-to-peak amplitudes of the Pt and Pd derivative spectra.

desorption in addition to AES to calibrate our film coverage. However, for Pt on Pd(110), both Pt and Pd readily adsorb CO and renders this method useless. We therefore use AES alone as a means of calibrating our Pt film coverages due to the lack of the availability of a complementary method.

We estimate the Pt to Pd Auger ratio for 1 and 2 monolayer films using equations which describe the variation of the substrate and overlayer signal intensity as a function of overlayer thickness (49). For this analysis we use an inelastic mean-free-path for the $\text{Pd}_{330}(\text{MNN})$ Auger electrons of 7 Å (50,51). For the $\text{Pt}_{64}(\text{NVV})$ Auger electrons we use an inelastic mean-free-path of 4 Å, the same as that which has been reported previously for the $\text{Au}_{69}(\text{NVV})$ Auger electrons (50,51). We feel this is valid due to the comparable kinetic energies for these Auger transitions. We also use handbook spectra for a measure of the peak-to-peak intensity ratio for bulk Pt and Pd (52). Using this method we obtain values for the Auger ratio of Pt to Pd of 0.34 and 0.71 for the first and second monolayers, respectively. We also compare our calculated values for the Pt to Pd ratio with values found for the first two layers of Pt on Pd(100) (2). In this study, well characterized Bragg intensity oscillations are used to determine the coverage calibration. The values obtained for the ratio of Pt to Pd was 0.30 for the first layer and 0.77 for the second layer (2). Both of these values agree quite well with the ratios of 0.4 and 0.8 suggested by the subtle breaks in the Auger data. We take this then as an indication of growth in a layer-by-layer manner, at least for the first two Pt layers. Subsequent

Pt coverages are based on these data. We estimate an uncertainty in Pt coverage of about $\pm 10\text{-}15\%$.

B. LEED Measurements

The overlayer superstructures are followed as a function of film thickness and annealing temperature via a video-LEED system (40). The Pt films are deposited by exposing the Pd crystal, held at the desired deposition temperature, to the Pt vapor flux. The resultant film thickness is determined by AES. After deposition, the sample is slowly heated to a desired temperature, held for 20 seconds at constant temperature to allow equilibration, and then quenched below 200 K where the LEED pattern is observed. The sequence is then repeated for the next annealing temperature. Diffraction spot profiles are recorded and processed with the video-LEED system (40).

1. Deposition at 300 K

We have measured the LEED intensity profiles for a series of Pt films as a function of annealing temperature following deposition at 300 K. The profiles are measured along the [001] (real space) direction between the (0,0) and (0,-1) beams at a beam energy of 35eV. For a coverage of 1 Pt layer a (1x1) diffraction pattern is observed, and no fractional order spots or streaking are detected. As the Pt film thickness is increased to 2 monolayers heavy streaking appears. For higher Pt coverages, we observe the appearance of additional fractional order beams that grow in intensity as the film is slowly annealed. These

data are displayed in Fig. 2. At a coverage of 2 Pt layers, Fig. 2(a), some intensity centered around the half-order position is evident after annealing to 370-400 K. The fractional-order intensity is very broad and is essentially featureless. The fractional-order streaking disappears after annealing to temperatures greater than 575 K. Following deposition of 3 Pt layers, Fig. 2(b), the same streaking appears after annealing to 370-400 K as was observed after annealing 2 monolayers of Pt to the same temperature. As the temperature is increased to 550 K the half-order spot increases in intensity and sharpens slightly. Increasing the temperature further results in a splitting of the half-order spot. The two components of the half-order spot diverge as the temperature is raised and reach third-order positions at 630 K. Annealing to temperatures higher than 630 K results in complete loss of the fractional-order components. The continuous splitting of the half-order spot as the film is annealed to higher temperatures, resulting in the development of a (1x3) superstructure, is more apparent for thicker Pt films as evident in Figs. 2(c) and 2(d). For 5 monolayers of Pt, Fig. 2(c), a broad half-order spot results after heating to 400 K, which then proceeds to split continuously as the temperature is further increased. After annealing to 760 K a full (1x3) superstructure has developed. Heating to temperatures higher than 760 K results in loss of the (1x3) and return of a (1x1) pattern. For 15 monolayers of Pt, Fig. 2(d), the broad half-order spot persists up to 600 K. For higher annealing temperatures the half-order spot begins to split, and a full (1x3) is attained after annealing to 885 K. Heating to temperatures higher than

Figure 2. LEED intensity profiles for Pt films deposited at 300 K as a

function of annealing temperature

Profiles are taken along the [001] (real space) direction

between the (0,0) and (0,-1) beams for a beam energy of 35 eV.

a) 2 layers of Pt

b) 3 layers of Pt

c) 5 layers of Pt

d) 15 layers of Pt

885 K results in a return of the (1x1) pattern. The continuous splitting of the half-order spot for the Pt films shows similarities to that which we observed for Au films on Pd(110) (4). However, for Au the degree of splitting seemed to depend only on the initial Au coverage, and did not change as a function of annealing temperature. The splitting observed for the Pt films appears to depend not only on coverage but on the annealing temperature as well.

From the profiles of Fig. 2, it appears that the temperature at which the half-order components begin to diverge continuously and the temperature at which they reach the third-order positions depends on the Pt film thickness. This coverage dependence of the diverging half-order components is shown graphically in Fig. 3, where ΔK_1 for the component which develops into the (0, -2/3) spot is plotted vs. temperature for the 3, 5, and 15 layer Pt films. The temperatures at which the half-order spots start to diverge are found to be 575 K for the 3 layer film, 655 K for the 5 layer film and 710 K for the 15 layer thick Pt film. The splitting for the 5 layer thick film is evident already at 460 K, but does not truly begin to diverge until 655 K. The temperature at which the (1x3) fully develops is also coverage dependent. The fractional order-components for the 3, 5, and 15 layer films attain their full third-order positions at 630, 760, and 885 K, respectively.

The spot splitting observed in the development of the (1x3) suggests a structural change is occurring for the Pt films as the temperature increases. A trend toward three-dimensional growth was speculated to be the basis for the (1x2) to (1x3) transition observed for Au films on

Figure 3. Plot of $\Delta K_{||}$ for the fractional-order component which develops into the $(0, -2/3)$ spot vs. annealing temperature for Pt films of 3, 5, and 15 monolayers

Pd(110) (4). If a structural change is occurring for the Pt films as the temperature is increased leading to the (1x2) to (1x3) transition, it may be possible to detect some change in the Pt Auger signal as this conversion takes place. Therefore, we have followed the Pt Auger signal intensity relative to that for Pd as the Pt films are slowly annealed. These data are shown in Fig. 4. Here we present a plot of the Pt/Pd Auger ratio as a function of annealing temperature for Pt films of 2, 3, 5, and 10 layers. The Pt film of 15 layers is not represented in this figure, since at this thickness the Pd Auger signal is completely attenuated, and a change in the Pt signal relative to Pd can not be measured. Data for a 10 monolayer film is substituted for the 15 monolayer results. It is evident that a decrease in the Pt/Pd Auger ratio does occur as the temperature increases. The onset of the reduction of the Pt/Pd ratio depends on the Pt film thickness, and the temperature at which the decrease begins is indicated for the different films by the vertical dashed lines of Fig. 4. These lines are drawn at the point at which the ratio first starts to decline. The observed reductions occur at temperatures of 550, 575, 630, and 710 K for the 2, 3, 5, and 10 layer films, respectively. The temperature at which the Pt/Pd ratio initially decreases agrees very well with the temperatures at which the half-order components, for films of comparable coverage, first begin to diverge as shown in Fig. 3 and 4. In addition it is apparent from the Auger data that when the loss of the fractional order beams occurs there has been a significant loss of the Pt Auger signal. These data indicate that a morphological change is occurring in the Pt films as

Figure 4. Variation of the $\text{Pt}_{64}(\text{NVV})$ to $\text{Pd}_{330}(\text{MNN})$ Auger peak ratio versus annealing temperature for a series of Pt films, deposited at 300 K, varying in thickness from 2 to 10 monolayers

the temperature increases and is in someway connected with the transition of the (1x2) to (1x3) structures. We will further discuss the details of this transition in section IV.

2. Variation of deposition temperature, 130-300 K

In addition to studying Pt films deposited at 300 K, we have looked at the effect of deposition temperature on the evolution of the LEED superstructures. We find that for deposition temperatures below 200 K we can stabilize the (1x2) structure, and that the stabilization of the (1x2) is coverage dependent. A sharp and intense (1x2) develops upon annealing to ca. 410 K, only if the film is 3 monolayers deep and is deposited between 130 and 200 K. If the same amount of Pt is deposited at higher substrate temperatures, a (1x3) always develops upon annealing. At all higher Pt coverages, annealing brings on the (1x3) structure, independent of the deposition conditions. The dependence of the (1x2) and (1x3), on the deposition temperature is displayed in Fig. 5. Here we show intensity profiles measured along the [001] (real space) direction between the (0,0) and (0,-1) beams at a beam energy of 35 eV. The profiles of Fig. 5 demonstrate the evolution of the superstructures as a function of annealing temperature following deposition of 3 layers of Pt at 130, 170, 200, 225, and 300 K. After deposition at 130 K, Fig. 5(a), a sharp and intense (1x2) develops upon annealing. The intensity and sharpness of the (1x2) far exceeds that observed after deposition at 300 K, where a broad (1x2) forms after low temperature annealing and prior to spot splitting (see Fig. 2). The (1x2) is stable up to 650 K. Annealing

Figure 5. LEED intensity profiles for 3 layer Pt films deposited between

130 and 300 K as a function of annealing temperature

Profiles are taken along the [001] (real space) direction

between the (0,0) and (0,-1) beams for a beam energy of 35 eV.

a) $T_{\text{deposition}} = 130 \text{ K}$

b) $T_{\text{deposition}} = 170 \text{ K}$

c) $T_{\text{deposition}} = 200 \text{ K}$

d) $T_{\text{deposition}} = 225 \text{ K}$

e) $T_{\text{deposition}} = 300 \text{ K}$

to higher temperatures results in a loss of the half-order beam intensity and subsequently a complete loss of the (1x2) by 740 K. As the deposition temperature increases to 170 and 200 K, Fig. 5(b) and 5(c) respectively, the (1x2) still develops upon annealing, although the full width half maximum (FWHM) of the half-order spot increases. Again, as for deposition at 130 K, the (1x2) is stable up to 650 K for deposition at 170 and 200 K. Increasing the deposition temperature to 225 K, Fig. 5(d), we find that following annealing to 530 K, the half-order spot begins to split, similar to that found for deposition at 300 K. However, the (1x3) never fully develops and the split half-order spot is lost after annealing to 650 K. Deposition at 300 K is shown again in Fig. 5(e), where the half-order spot splits continuously and the full (1x3) develops at 580 K. As mentioned previously, as the deposition temperature increases from 130 up to 200 K, an increase in the FWHM of the half-order spot is observed. This increase in the FWHM is shown in Fig. 6 as a function of deposition temperature. The data shown in Fig. 6 are taken from the profiles obtained after annealing to 470 K. As is evident, there is a steady increase in the FWHM as the deposition temperature is raised from 130 to 225 K. Since the (1x2) to (1x3) transition is dependent on the deposition temperature, we use Auger again to see if the deposition temperature has any measurable effects on the stability of the Pt films.

We have measured the Pt Auger intensity relative to Pd as a function of annealing temperature for the 3 monolayer films which have been deposited at temperatures between 130 and 225 K. The results of these

Figure 6. Variation of the FWHM of the half-order spot for 3 layer Pt films as a function of deposition temperature, measured after annealing the films to 470 K

Figure 7. Variation of the $\text{Pt}_{64}(\text{NVV})$ to $\text{Pd}_{330}(\text{MNN})$ Auger peak ratio versus annealing temperature for a series of 3 layer Pt films deposited at deposition temperatures ranging from 130 up to 225 K

measurements are shown in Fig. 7. The first significant decrease in the Auger ratio for the sets of data shown is indicated by the vertical dashed lines of Fig. 7. There does appear to be a slight difference in the onset of the decrease in the ratio for the different deposition conditions. The film deposited at 130 K, for which the sharpest (1x2) develops upon annealing, appears to be the most stable. The Pt/Pd ratio for this deposition temperature does not start to decrease until 640 K. For the higher deposition temperatures, 170-225 K, all appear to decrease after annealing to 530 K. This is over 100 K less than that observed for deposition at 130 K. The decline in the ratio for these higher deposition temperatures are not distinguishable from one another. Either Auger is not sensitive enough to distinguish a difference, or more likely the frequency of our measurements are not high enough to permit a differentiation in the decrease in the ratio for these higher deposition temperatures. The temperature range for which the decrease in the Pt Auger signal occurs for deposition at 130 K is 600 ± 30 K, based on 5 separate measurements. The temperature range in which a decrease is observed for all other deposition temperatures is 540 ± 30 K. This latter range is based on 8 separate measurements covering deposition temperatures from 170 to 300 K. This strongly suggests that films deposited at 130 K are more stable. In any case, we find that a good (1x2) structure can be stabilized by annealing a film 3 layers thick which has been deposited at 130 to 200 K. Auger results indicate that the film deposited at 130 K is more stable than those deposited at higher deposition temperatures. For a constant coverage of 3 layers, as the

deposition temperature increases (170-200 K), the half-order spot broadens. For deposition at 225 K the half-order spot shows signs of splitting, and by 300 K has fully developed into the (1x3). Low temperature deposition and 3 monolayers of Pt are the only conditions under which the (1x2) can be stabilized. At all higher Pt coverages, annealing brings on the (1x3) structure, independent of the deposition conditions.

C. Effects of CO and H₂ Adsorption on the Superstructures

We have found that the Pt films can form either (1x2) or (1x3) superstructures depending on the coverage and conditions of deposition. Similar (1x2) and (1x3) structures have been reported for bulk Pt(110) (20,23-25,27,36), although a transition between the two phases such as we describe has never been reported in the literature. Since Pt and Pd are known to form a continuous series of solid solutions (53,54), and the transformation of the (1x2) to the (1x3) occurs simultaneously with a decrease in the Pt/Pd Auger ratio (see Fig. 4), there exists the question of ordered alloy formation. That is, are the (1x2) and (1x3) superstructures true surface reconstructions, or do they result from an ordered Pt-Pd alloy which forms on annealing? No evidence of ordered bulk alloys exist for the Pt-Pd system (53,54), although very limited data are available. However, we can use a very simple approach to test the origins of the (1x2) and (1x3) superstructures.

It is well known for the (1x2) (27), and has been shown for the (1x3) (23) structures observed on bulk Pt(110) surfaces, that adsorption

of certain gas molecules, namely CO, "lifts" the reconstructions. That is, adsorption of CO at a temperature of 300 K reverts the (1x2) (27), while adsorption of CO at 300-400 K reverts the (1x3) (23) back to the unreconstructed (1x1) phase. This conversion is found to be fully reversible, and heating to temperatures high enough to desorb the CO molecules results in the return of the (1x2) or (1x3) superstructures (23,27). We have therefore used CO adsorption as a means of testing whether the (1x2) and (1x3) structures observed are true surface reconstructions. The results of these experiments are shown in Fig. 8. Here we show LEED profiles for the both the (1x2) and the (1x3) superstructures as a function of CO exposure in Langmuirs (L). As is obvious from the data of Fig. 8, both the (1x2) and the (1x3) structures can be lifted with CO, and in addition the structures return when CO desorbs. The complete "lifting" of the (1x2) structure, Fig. 8(a), is activated at an adsorption temperature of 380 K, and is completely gone after a 2.0 L exposure. The "lifting" of the (1x3) structure, Fig. 8(b), is activated at a slightly higher temperature, 430 K, and is completely gone following a 2.5 L exposure. If the (1x2) and (1x3) structures were due to an ordered Pt-Pd alloy, it would be highly unlikely that adsorption of CO would disorder the alloy and cause a change to the (1x1) structure. We therefore believe that we can classify the (1x2) and (1x3) superstructures as true surface reconstructions, similar to the (1x2) and (1x3) missing row reconstructions which have been reported for bulk Pt(110) surfaces (20,23-25,27,36).

In section III(B) we described the effects of deposition temperature

Figure 8. Intensity profiles of the Pt film superstructures as a function of CO exposure in Langmuirs (L)

The profiles demonstrate the lifting of the structures by the adsorption of CO.

a) (1x2) superstructure, $T_{\text{adsorption}} = 380 \text{ K}$

b) (1x3) superstructure, $T_{\text{adsorption}} = 430 \text{ K}$

on the evolution of the superstructures. We find that the (1x2) can be stabilized by depositing 3 layers of Pt at 130-200 K. Higher deposition temperatures, for the same coverage, result in a splitting of the half-order spot and formation of the (1x3). This deposition temperature dependence between 130 and 225 K raises the question of interference in the growth of the film due to adsorption of background contaminants. Pd is known to have a high affinity for hydrogen, and in addition, the desorption spectra for hydrogen from Pd(110) (55) show low temperature features which occur in the same temperature range. We know that in the time it takes to prepare our films, 20-30 minutes, some hydrogen must adsorb from the background. Hydrogen is the dominant background component under ultra-high vacuum conditions due to permeation through the stainless steel walls of the system. It is therefore possible that differing hydrogen concentrations on the Pd surface resulting from the different Pt adsorption temperatures in some way affect the growth of the Pt films. It has been shown previously that adsorption of certain gases can significantly alter the growth of metal films (56). We therefore try to quantitate the amount of hydrogen present on the surface under the different deposition conditions and relate this to our results.

We first measure the amount of hydrogen adsorbed on our Pd surface following a 30 minute exposure to background conditions, 2×10^{-10} Torr, at adsorption temperatures of 130, 170, 200, 225, and 300 K. This is a typical length of time require to prepare the Pt films. We use thermal desorption spectroscopy, and comparisons with previously published H desorption data from Pd(110) (55), as a means of quantitating the

hydrogen concentrations. Previous work (55) indicates that the adsorption of 1 monolayer of hydrogen atoms, i.e., equal numbers of H and top most Pd surface atoms, corresponds to the maximum of the (2x1) H LEED structure and the onset of the low temperature α -desorption states. We use the onset of the α_2 desorption state and LEED as means of calibrating the saturation of the H monolayer, which corresponds to 9.35×10^{10} H atoms/cm² for the Pd(110) surface. Shown in Fig. 9 are the results obtained after exposing the Pd crystal to background pressures (2×10^{-10} Torr) for 30 minutes, at a variety of adsorption temperatures. The amount of hydrogen present after the 30 minute exposure at 130 K is found to be on the order of 0.33 monolayers. For higher adsorption temperatures the hydrogen concentration is slightly smaller, ranging from 0.29 to 0.31 monolayers for adsorption temperatures between 170 and 225 K. For all practical purposes the hydrogen concentration is essentially constant over the temperature range of 130 to 225 K, those temperatures for which we observe the start of the (1x2) to (1x3) transition in the Pt film reconstruction. The amount of hydrogen which adsorbs from the background is never enough to observe any H LEED structures or the well known H induced (1x2) reconstruction of the Pd(110) surface (55). In any case, hydrogen adsorption from the background does not appear to vary significantly over the temperature range for which we observe the transition in temperature dependence of the Pt film structures.

If H adsorbed from the background was stabilizing the (1x2) it is possible that higher H concentrations may enhance the quality of the (1x2) pattern observed for the Pt film reconstruction at $T_{\text{deposition}} = 130$ K,

Figure 9. Measure of the hydrogen coverage on Pd(110) following 30 minute exposures to background conditions, 2×10^{-10} Torr, as a function of adsorption temperature
Coverages given are based on TDS and LEED measurements.

or may even stabilize the (1x2) for Pt adsorbed at higher temperatures, $T_{\text{deposition}} = 225$ K. To satisfy our curiosity and to be sure that the somewhat higher H concentration found for lower adsorption temperatures is not contributing to the low temperature stabilization of the (1x2), we have deposited Pt films on H predosed Pd to test for any H induced effects. We conduct these experiments by first adsorbing 1.2 monolayers of H at both 130 K and 225 K and then depositing 3 monolayers of Pt on top of the H predosed surface. We use 1.2 monolayers of H because we find this corresponds to the amount of H necessary to saturate the surface for adsorption at 225 K. The results of these experiments are shown in Fig. 10. It is obvious that increasing the H concentration has little effect on a Pt film adsorbed at 130 K, Fig. 10(a). We still observe the (1x2) structure after annealing. A slight decrease in intensity is evident for the H predosed film which could result from a variety of different reasons other than the presence of the H, a variation of beam current from experiment to experiment being the most probable. Likewise, a higher H concentration on the Pd prior to adsorption of Pt at 225 K, Fig. 10(b), has no noticeable effect on the superstructure observed after annealing the Pt film. These results show convincingly that H predosed at exposures three times that observed for background adsorption does not significantly alter the development of the (1x2) or (1x3) superstructures for adsorption at 130 and 225 K. We therefore do not believe H contamination contributes in any way to the stabilization of the (1x2) for Pt adsorption at low temperatures.

Figure 10. Effect of hydrogen adsorption on the (1x2) and (1x3) superstructures following deposition of Pt on clean Pd(110) (Pt/Pd), and following deposition of Pt on Pd(110) predosed with 1.2 monolayers of H (Pt/H₂/Pd)

a) 3 layers of Pt deposited at 130 K, annealed to 640 K.

b) 3 layers of Pt deposited at 225 K, annealed to 640 K.

IV. DISCUSSION

We have completed a detailed study of the growth, structure, and thermal stability of Pt films grown on Pd(110) under a variety of deposition conditions. We shall now discuss the results obtained. The growth mode of the Pt film, the reconstruction and temperature dependence of the reconstruction, and mechanisms which may explain our results will be addressed. We shall finish with a comparison of the results obtained for Pt films on Pd(110) with those obtained for the growth of Au films on Pd(110) (4).

A. Growth of Pt on Pd(110)

If we look at the Pt-Pd system in terms of the classical theory of metal film growth a slight tendency for three-dimensional growth may be expected. As proposed over 30 years ago by Bauer (57), equilibrium film growth processes should rely on three thermodynamic factors: the surface energy of the substrate γ_s , the surface free energy of the film γ_f , and the interfacial energy γ_i . The surface free energies of the substrate and film can be obtained from calculations for bulk surfaces (58) or from experimental results (59). The interfacial energy term, however, is less accessible. This energy term reflects contributions, for example, from strain induced by lattice mismatch and/or such factors as heat of mixing of the film and substrate, both of which are factors which may add to or subtract from the stability of the interface. Contributions from the interfacial energy are often assumed to be small compared to the

differences in surface energies and are many times ignored. If γ_f is less than γ_s , and γ_i is thought to be small, layer-by-layer (Frank-van der Merwe) growth is expected. If on the other hand γ_f is greater than γ_s , agglomeration of the overlayer is thought to occur to expose as much of the substrate metal as possible, and thus reduce the overall energy of the system. This is commonly referred to as Volmer-Weber growth, or growth as three-dimensional crystallites. Stranski-Krastanov growth (layer growth followed by agglomeration) occurs when contributions from the interfacial energy term becomes significant. That is, the film will tend to initially grow layer-by-layer up to a critical coverage where the interfacial energy contributions result in a break down of the layered growth of the system. We can use these criteria proposed by Bauer (57) to help predict the growth mechanism of Pt films on Pd(110).

The surface free energy of Pt, 2.69 J/m^2 (58) (2.20 J/m^2 (59)) is slightly greater than that for Pd, 2.04 J/m^2 (58) (1.74 J/m^2 (59)) which may produce a slight tendency for three-dimensional growth (58).

(Experimental values of surface free energies are given in parentheses.) However, the small lattice mismatch of 0.8% and the ability of these two metals to alloy at high temperatures (53,54), suggesting a possible attractive interaction between Pt and Pd, may act to reduce the interfacial energy enough to offset the differences in the free energies of these two metals. The ability of Pt to grow layer-by-layer on Pd(100) at room temperature (1,2) is evidence in favor of layer-by-layer growth for Pt on Pd(110), at least for the first few layers. However, the differences in the surface structure for the (100) and (110) surfaces may

introduce additional factors which could alter the growth processes for these two systems as suggested by a recent report by Fenter and Gustafsson (60).

We have attempted to determine the growth mode of the Pt films at 300 K, using Auger by monitoring the $Pt_{64}(NVV)$ and $Pd_{330}(MNN)$ transitions as a function of deposition time. However, the apparent absence of clear delineating segments in the data render our results ambiguous in their meaning. Previously published results for the growth of Pt on Pd(100) (1,2) indicates layer-by-layer growth for at least the first three layers for this system. Even though layer-by-layer growth was found for Pt on Pd(100) (1,2), clear delineating segments were not evident in the AES results. We cannot draw any firm conclusions about the growth mode of the Pt films on Pd(110) from the Auger results of Fig. 1. However, growth in a layer-by-layer manner can not be ruled out by these data.

Our calculations given in section III(A), for which we estimate the Pt to Pd Auger ratio for the first two layers assuming layer-by-layer growth, does give some supporting evidence in the determination of the mode growth of the Pt films. Using equations which describe the variation of the substrate and overlayer signal intensity as a function of overlayer thickness (49), we obtain values for the Auger ratio of Pt to Pd of 0.34 and 0.71 for the first and second monolayers, respectively. Both of these values agree quite well with the ratios of 0.4 and 0.8 suggested by the subtle breaks in the Auger data, and with the ratios reported for the first two layers of Pt on Pd(100) (2), a system which is known to grow layer-by-layer. From our results we speculate that the

growth of Pt on Pd(110) is essentially layer-by-layer for the first two layers. Our results do not unequivocally point to a layer-by-layer mode of growth for deposition at 300 K, although gross islanding or agglomeration are not suggested by the data either.

B. Pt Film Reconstruction

To begin our discussion of the reconstructions of the Pt overlayers we start with a basic review of the reconstruction of the (110) surface. The (1x2) and (1x3) reconstructions fall into the category referred to as "missing row" reconstructions. That is, in the case of the (1x2) every other row along the [001] direction is missing. This change in periodicity from the unreconstructed (1x1)-(110) surface to the (1x2) and the (1x3) surfaces is displayed in Fig. 11. The model for the (1x2) "missing row" reconstruction, Fig. 11(b), is quite well accepted. The (1x3) reconstruction, although observed less frequently, is also thought to fall into the category of a "missing row" reconstruction (23). A model for the (1x3) is shown in Fig. 11(c). In contrast to the reconstruction of the more atomically smooth (111) and (100) surfaces the reconstruction of the (110) surface involves a transition to a micro-faceted surface, with (111) micro-facets along the trough walls (61). The difference between the (1x2) and (1x3) lies in the degree of facetting.

We observe both (1x2) and (1x3) structures in our Pt films, their formation depending on the film coverage and deposition conditions. As discussed in section III(B) we believe that the (1x2) and (1x3)

Figure 11. Schematic representation of the (110) unreconstructed and reconstructed surface

- a) Unreconstructed (1x1)
- b) Reconstructed (1x2)
- c) Reconstructed (1x3)

superstructures observed are due to true missing row reconstructions, similar in nature to those which have been reported for the surface of bulk Pt(110) (20,23-25,27,36). Both the (1x2) and (1x3) superstructures of the Pt films are found to revert to the (1x1) structure upon adsorption of CO. The lifting of the (1x2) and (1x3) are found to be fully reversible with the (1x1) when CO adsorbs and desorbs from the surface. These results are identical to those reported for the interaction of CO with bulk Pt(110) (1x2) and (1x3) surface reconstructions (23,27). We therefore believe that the (1x2) and (1x3) structures are due to the reconstruction of the Pt films, and are not due to the formation of an ordered surface alloy of Pt and Pd.

1. Reconstruction following deposition at 300 K

As we reported in section III(B), we observe the formation of a (1x3) superstructure following annealing of films which are 3 layers thick or greater and are deposited at 300 K. Following deposition of these films, a broad half-order spot develops after annealing to temperatures around 450 K. As the films are heated to higher temperatures, the half-order spot splits continuously as a function of temperature until a full (1x3) pattern develops. These results show similarities to the reconstruction of Au films on Pd(110) (4). For the latter system we found that the (1x3) evolves from the (1x2) by the continuous splitting of the half-order spot, but only as the Au coverage is increased. In contrast, for the Pt films the degree of splitting increases, under conditions of constant coverage, as the film is annealed

to higher temperatures.

We explained the splitting phenomenon for the Au films (4) as being due to the coexistence of random (1x2) and (1x3) regions, each being smaller than the coherence length of the LEED optics. The relative concentrations of these phases was then dependent on the film coverage, with the (1x3) favored at higher coverages. The transition to the (1x3) for the Au films (4) was not due to an electronic perturbation from the Pd substrate, but instead can be attributed to the formation of antiphase domains for the (1x2) phase which result in the formation of (1x3) channels. If we look at the pure (1x2) phase, the periodicity repeats every second lattice spacing. This periodicity provides the opportunity for the existence of antiphase domains, that is, (1x2) domains displaced by one lattice spacing along the [001] direction. If we look at a structural model of an antiphase domain boundary for a pure (1x2) phase, we find that the boundary results in the formation of a (1x3) channel. This formation of a (1x3) channel at the antiphase domain boundary of a pure (1x2) phase is represented schematically in Fig. 12. In this picture a pure (1x2) phase is shown in Fig. 12(a), and the formation of an antiphase domain is represented in Fig. 12(b). We can see that the (1x2) phase at the left side of the lattice model of Fig. 12(b) is out of phase with the (1x2) phase on the right side of the lattice model by a single lattice spacing. At the domain boundary, two consecutive rows are missing resulting from the continuation of the "missing row" arrangement for each respective domain. The displacement of these consecutive rows results in the formation of a (1x3) channel at the domain boundary as

Figure 12. Schematic representation of the formation of a (1x3) channel at an antiphase domain between two (1x2) phases

evident in Fig. 12(b). The existence of antiphase domains can explain the development of the (1x3) phase for the Au films (4). We know that as the Au coverage increases past 2 monolayers a transition to three-dimensional growth occurs resulting in a disruption in the long range order (smoothness) of the film and thus an increased probability for the formation of antiphase domains. As coverage increases so should the degree of disorder, and therefore at some point the density of (1x3) channels from the antiphase domains may become the majority species. This would then give rise to a (1x3) diffraction pattern.

This same explanation for the formation of the (1x3) from the (1x2) can be applied to the Pt on Pd(110) system. For the Pt films this transition is found to be purely temperature dependent. The temperature dependence of the (1x2) to (1x3) transition can be explained for the Pt films by recalling the data presented in Fig. 4. It is evident from Fig. 4 that a decrease in the Pt/Pd Auger ratio occurs as the Pt films are heated to higher temperatures, the onset of the reduction of the Pt/Pd ratio depending on the Pt film thickness. The temperature at which the initial decrease of the Pt/Pd ratio occurs agrees very well with the temperatures at which the half-order components, at least for the low coverage regime, first begin to diverge as shown in Fig. 13. In this figure the temperature at which the splitting of the half-order spot begins, the initial loss of Pt in AES, and the first loss of the fractional order spots are plotted as a function of Pt film thickness. For the 3 and 5 monolayer thick films, the splitting of the half-order spot and the initial loss of Pt in the Auger spectrum are essentially

Figure 13. Initial splitting of the half-order spot, loss of the Pt Auger signal, and loss of fractional-order spot intensity as a function of film thickness and temperature

identical. For the data shown in Fig. 13 for the 15 layer film the half-order spot splits long before any loss of Pt is observed. However, this is most likely due to the severe loss in sensitivity of Auger to the interface for a film of this thickness.

As suggested previously in section III(B) these data seem to indicate that changes are occurring in the Pt films as the temperature increases which are in some way connected with the transition of the (1x2) to (1x3) structures. As commented on earlier in section IV(A), circumstances do exist for the Pt-Pd system which may favor three-dimensional growth of the film under equilibrium conditions, i.e., higher temperatures. The films may grow layer-by-layer like at room temperature, and slowly agglomerate when heated. Such a transformation is suggested for the Pt-Pd(110) system by the Auger results of Fig. 4. If the flat films do begin to decompose and agglomerate as the temperature is increased, a decrease in the Pt/Pd Auger ratio would be expected, as is evident in Fig. 4. However, dissolution of the Pt films could also explain the loss of the Pt Auger intensity. Although, if this decrease in the Pt signal was due to dissolution of the Pt into the Pd substrate, one may not expect the reduction in the Pt signal to be coverage dependent. That is, dissolution at the interface should occur at the same temperature regardless of the overlayer thickness as was found for Au films on Pd(110) (4). For the case of agglomeration a coverage dependence would be expected due to kinetic limitations in the rearrangement of the thicker films. However, it must be remembered that the sensitivity of Auger to changes occurring at the interface may be

thickness dependent. Therefore, this argument should only hold true in the low coverage regime, ≤ 5 layers. No thickness dependence in the Auger ratios as a function of temperature was observed for the dissolution of Au films into Pd(110) (4) in this coverage regime, ≤ 5 layers.

We therefore believe for Pt on Pd(110), as was the argument for Au on Pd(110) (4), that the transition of the (1x2) to (1x3) results from a slow break down of the smoothness of the films. In the case of Pt this occurs as the films are annealed to higher temperatures. The initial break down results from the differences in surface free energies between Pt and Pd, 2.69 J/m^2 (58) (2.20 J/m^2 (59)) and 2.04 J/m^2 (1.74 J/m^2 (59)) respectively, which favor agglomeration of the film under equilibrium conditions. However, dissolution in addition to agglomeration probably occurs to some degree as the temperature increases. The three-dimensional growth (and some degree of dissolution) which occurs as the films are annealed results in a disruption in the long range order (smoothness) of the films, and thus an increased probability for the formation of antiphase domains as was the argument for Au films on Pd(110) (4). We have shown previously in Fig. 12 that (1x3) channels form at the antiphase domain boundaries. Therefore, as the temperature increases so should the degree of disorder, and at some point the density of (1x3) channels from the antiphase domains become the majority species. This would then give rise to a (1x3) diffraction pattern.

2. Reconstruction following deposition at 130-300 K

In addition to studying Pt films deposited at 300 K, we have looked at the effect of deposition temperature on the evolution of the LEED structures. We find that for deposition temperatures below 200 K we can stabilize the (1x2) structure, and that the formation of the (1x2) is coverage dependent. A sharp and intense (1x2) develops upon annealing to ca. 410 K, only if the film is 3 monolayers deep and is deposited between 130 and 200 K. If the same amount of Pt is deposited at higher substrate temperatures, a (1x3) always develops upon annealing. At all higher Pt coverages, annealing brings on the (1x3) structure, independent of the deposition conditions.

There are two possible models which may serve to describe the deposition temperature dependence for the Pt film reconstructions. We refer to them as the "roughening" model and the "smoothing" model. Each, as their names imply, refer to the roughening or smoothing of the films as deposition temperature increases. The basis for the "roughening" model comes from the proposed thermodynamic drive toward three-dimensional growth as the system moves toward equilibrium (57). The "smoothing" model is based on an increased Pt atom mobility as temperature increases and a possible attractive interfacial energy for Pt and Pd which may act to smooth the film (2). We first discuss our results in terms of the "roughening" model since it is most consistent with our discussion thus far.

The deposition temperature dependence observed for the stabilization of the (1x2) for the 3 layer Pt films may be explained by the

"roughening" model which consists of a combination of thermodynamic and kinetic effects which control the film growth at the Pt-Pd interface. As we discussed in section IV(B), thermodynamic factors (free energy differences) may force a break up in the two-dimensional order (smoothness) of the films as the temperature increases and equilibrium is approached. In addition, low temperature deposition may act to kinetically limit this transition to three-dimensional growth due to a reduced adatom mobility. It is therefore possible that for deposition at 130 K the film is kinetically trapped into a smoother, more continuous film. Heating this film to temperatures greater than 300 K activates the (1×2) reconstruction of the film. Due to the better layer-by-layer quality following deposition at 130 K the long range order of the (1×2) which forms is higher, and therefore the film produced under these conditions is more stable. This is supported by the data of Fig. 7, which shows that the film deposited at 130 K is stable to higher temperatures than those films deposited at higher substrate temperatures. Deposition at higher substrate temperatures allows diffusion of the adatoms and results in some microscopic disruption in the two-dimensionality of the film. This disruption in the two-dimensionality results from roughness induced by the film's thermodynamic drive toward three-dimensional growth. A steady increase in the two-dimensional disorder of the films deposited at higher substrate temperatures is suggested by the uniform increase in the FWHM of the half-order spot with deposition temperature as shown in Fig. 6. As the deposition temperature increases diffusion increases accordingly, and therefore the drive toward

three-dimensional growth should also be enhanced.

The critical coverage of 3 monolayers found for this temperature dependent transition may be caused by a substrate overlayer interaction which is coverage dependent. Remember that for all Pt coverages greater than 3 layers, annealing brings on the (1x3) structure, independent of the deposition conditions. It is possible that the improved layer-by-layer growth, and thus the stabilization of the (1x2) found following deposition of 3 layers of Pt at 130 K, is not only favored by the low diffusion of adatoms at low temperature, but also by an attractive interaction between the Pt atoms and the Pd substrate. This infers that there exists an activation barrier to overcoming this attractive force, and this activation barrier can be overcome by depositing at higher substrate temperatures. The diffusion of the Pt adatoms may not only depend on the temperature-dependent diffusivity, but on the extent of this attractive interaction as well. Therefore, as the film thickness increases and the Pt atoms at the surface get further away from the Pt-Pd interface, this attractive force can break down. This break down would tend to increase the tendency toward three-dimensional clustering of the Pt atoms for higher coverages but similar deposition temperatures. An increase in the three-dimensional nature of the Pt at higher film coverages would result in an increase in the two-dimensional disorder of the films even for deposition at 130 K. This coverage dependent disorder then results in an increased tendency toward three-dimensional growth as the temperature is increased, and thus the formation of the (1x3) even for the thicker films deposited at 130 K. All the data presented thus

far are consistent with the "roughening" model.

The alternative model is that which we call the "smoothing" model, and can also be used to explain the deposition temperature dependence of the (1x2) and (1x3) reconstructions. Recall, the "smoothing" model is based on a higher adatom mobility for higher deposition temperatures and an attractive interfacial energy term for the Pt-Pd system. It is known for the Pt on Pd(100) system (2) that growth is layer-by-layer, and that increasing the deposition temperature increases the layer-by-layer quality of the film due to an increased adatom mobility. Since the only difference between Pt on Pd(100) and Pd(110) is the substrate morphology, one might assume that energetic forces such as interfacial energies may be similar, and that growth processes for the two systems may likewise be similar. That is, an increase in the deposition temperature for Pt on Pd(110) may also serve to smooth the film giving it a better layer-by-layer quality. We thus refer to this as the "smoothing" model. For the "smoothing" model we make some simple assumptions: (1) the Pt films are rougher at lower deposition temperatures than at higher temperatures; (2) both the (1x2) and (1x3) require areas of the film which are three layers deep; (3) the (1x3) requires a larger area for nucleation than does the (1x2); and (4) reconstruction occurs (starts) before large scale diffusion kicks in significantly. The first assumption is rather straight forward, and originates from the proposed poorer layer-by-layer quality at low temperatures for Pt on Pd(100) (2). The second assumption is set by our experimental data, while the assumption of a larger area for nucleation of the (1x3) is based on a larger unit cell for this

reconstruction relative to the (1x2). The last assumption is required to support the model. We now apply the "smoothing" model to our experimental results.

For low temperature deposition of a Pt film 3 layers thick, $T_{\text{deposition}} = 130$ K, the film will be rather rough with areas of the film that are less than three layers deep and areas that are more than three layers deep. The rougher the film, the smaller the average area of 3 layer thick regions will be. If, as we assume, the (1x3) requires a larger area for nucleation than the (1x2) it is possible that at this low deposition temperature the average area of the film which is 3 layers thick is too small to nucleate the (1x3). However, under these conditions the (1x2) can nucleate and is therefore the stable phase for deposition at 130 K. As deposition temperature increases, the average area of the film which is three layers thick increases, and in some areas the critical nucleation size required for the (1x3) has been reached, allowing this phase to exist together with the (1x2). As deposition temperature increases, the (1x3) regions grow at the expense of the (1x2) regions, and by 225 K the (1x3) is the majority species. Also remember that for all films thicker than 3 layers the (1x3) forms, independent of the deposition conditions. This most likely results from an increase in the average area of film which is 3 layers thick for these higher coverages, even for low temperature deposition. This explanation is consistent with the "smoothing" model.

Although both models serve to explain the (1x2) and (1x3) temperature dependence, the "roughening" model is most consistent with

our results, and results for bulk reconstructions. The only experimental results, however, which truly favor the "roughening" model over the "smoothing" model lies in the behavior of the Pt Auger signal as the half-order LEED beam splits to third-order beams. The splitting is found to occur simultaneously with a decrease in the Pt Auger signal, signifying either agglomeration and/or dissolution of the film. If this transition was due to a smoothing of the film, which caused the (1x3) to grow at the expense of the (1x2), then either a constant Pt/Pd Auger ratio or a slightly higher ratio would be expected with increasing temperature as the Pt film becomes more continuous. The decrease in the Pt/Pd Auger ratio which we observe during this transition is more consistent with the proposed "roughening model. For the "smoothing" model it is assumed that reconstruction occurs before diffusion becomes significant. However, reconstruction of bulk Pt begins at 315 K (62) and also occurs around 300 K for the Pt films as indicated by our LEED results. Therefore, it is difficult to believe that by 300 K, diffusion would not become significant enough to smooth the films deposited between 130 and 225 K by the same degree. For the assumption that reconstruction begins before significant diffusion occurs to be true, would require an "electronic" locking in of the reconstruction at low temperatures before an actual physical reconstruction could occur. The "smoothing" model favors the (1x3) rather than the (1x2) as the more stable phase. The (1x3) structure for bulk Pt, however, could only be stabilized following high temperature oxygen treatments, implying that the (1x3) only forms following some perturbation of the clean Pt(110) surface (20,23). In

addition, the (1x3) (or higher order reconstructions) were found to occur on the Au(110) surface in regions of significant disorder (61).

Therefore, previous studies (20,23,61) are in favor of the (1x2) being the more stable phase, with the (1x3) occurring as disorder of the system increases. The "roughening" model is consistent with this picture. The "smoothing" model was originally proposed because the substrate morphology was assumed to have no major effect on the film growth mode. That is, one might assume that the energetic forces such as interfacial energies may be similar for the growth of Pt on Pd(110) as for Pt on Pd(100) (2) and the two systems would thus behave similarly. However, a recent publication by Fenter and Gustafsson (16) for the growth of Au on Ag(110) indicates that this may not be true. They find that Au grows in a "bilayer" Volmer-Weber mode on Ag(110) whereas Au on Ag(111) (63) and Ag(100) (64) grows layer-by-layer. They believe that the most likely explanation for the "bilayer" growth is due to microscopic factors involving the open geometry of the (110) surface. The "roughening" model would be consistent with a trend toward multilayer growth with increasing temperature as was found for Au on Ag(110) (16). Although no hard experimental evidence is available to unequivocally rule out one model over the other, most evidence favors the "roughening" model. Techniques which would be more sensitive to the three-dimensional quality of the films, such as medium-energy ion scattering or scanning tunneling microscopy, would need to be employed to resolve this question. However, due to the evidence in favor of the "roughening" model we adopt this model for use in further discussion.

We believe that the temperature dependence found for the transition of the Pt (1x2) and (1x3) structures results from a combination of thermodynamic and kinetic effects which control the film growth at the Pt-Pd interface consistent with our proposed "roughening" model. We have ruled out any contribution to the transition as originating from H contamination from the background as was discussed in section III(B). Evidence exists in the literature for an order-disorder transition of the Pd(110) surface (65). The onset of this order-disorder phase transition was found to occur at 230 K using diffractive scattering of thermal He atoms. Our results indicate that changes in the Pt films are occurring already at temperatures as low as 150-170 K as evidenced by the deposition temperature dependence of the Pt films. We believe that these temperatures are too low for the observed 230 K Pd(110) phase transition (65) to be contributing to our results. The explanation for the (1x2) to (1x3) deposition temperature dependent transition which is most consistent with our data, is an alteration in the film growth process for the different deposition conditions of the Pt films, resulting from a combination of thermodynamic and kinetic effects.

C. Comparison of Pt and Au films on Pd(110)

We would now like to compare and contrast our results obtained for this study of Pt films on Pd(110) with results we have obtained for the growth and reconstruction of Au films on Pd(110) (4). As we mentioned earlier for both of these systems we observe (1x2) and (1x3) reconstructions. The (1x3) structure in both systems evolves by the

continuous splitting of the half-order spot. For the Au films (4) the splitting of the half-order spot and development of the (1x3) is coverage dependent. In contrast, for the Pt films the degree of splitting increases, under conditions of constant coverage, as the film is annealed to higher temperatures. The coverage of the Pt film only seems to affect the temperature at which the complete (1x3) forms. We have proposed for both of these systems that the transition of the (1x2) to (1x3) results from a slow break down of the two-dimensional order (smoothness) of the films which favors the formation of (1x3) channels. These differences in the results for Pt and Au on Pd(110) can be traced to simple factors which are known to affect film growth processes.

If we try to predict the mode of equilibrium growth of the Au and Pt films on Pd basing our conclusions solely on surface free energy considerations, one would expect the Au films to grow layer-by-layer and the Pt films to agglomerate. The surface free energy of Au is lower than that of Pd, 1.63 J/m^2 (58) (1.50 J/m^2 (59)) compared to 2.04 J/m^2 (58) (1.74 J/m^2 (59)) for Pd, while the surface free energy of Pt, 2.69 J/m^2 (58) (2.20 J/m^2 (59)), is greater than that of Pd. If we now consider the differences in lattice constants and their effect on the interfacial strain for these two systems, one would expect larger contributions to the interfacial energy in the Au films as coverage increases and negligible effects in the Pt-Pd system. This is substantiated by the 4.8% lattice mismatch between Au and Pd and only a 0.8% mismatch between Pt and Pd. The large lattice mismatch in the Au-Pd system may result in a Stranski-Krastanov mode of growth. That is, at some critical film

thickness the contributions from the lattice strain will result in a break down of the layered growth. These predictions based on Bauer's criteria (57) are very similar to those which are suggested by our experimental results.

For Pt on Pd(110) our results suggest that layer growth can be stabilized at low temperatures (pseudo-Frank-van der Merwe), while annealing causes a slow continuous agglomeration of the overlayer. For the Au films our results indicate a Stranski-Krastanov growth mode with a critical film thickness of 2 monolayers (4). This type of a growth mode has been suggested previously for Au on Pd(111) (66-68). These studies (66-68) also indicate a critical film thickness of 2 Au layers. Our experimental results do seem to follow those growth mechanisms predicted by Bauer's criteria for equilibrium growth (57). These different growth modes for the Au and Pt films can be used to explain the coverage dependence of the (1x2) to (1x3) films structures for the Au films and the temperature dependence of this transition for the Pt films.

We have proposed for both of these systems that the transition of the (1x2) to (1x3) results from a slow break down of the two-dimensional order (smoothness) of the films which favors the formation of (1x3) channels. In the case of Au this break down occurs because of the strain induced by the 4.8% lattice mismatch of the system. Heating the Au films to higher temperatures does not allow these defects to anneal out and does not result in any other morphological rearrangement of the film other than reconstruction. Therefore once the film is deposited, heating causes reconstruction of the Au, but disorder is locked in by the defect

structure of the film so that the spot splitting remains constant. That is, as the film is annealed to higher temperatures the relative populations of (1x2) and (1x3) regions does not change. As the Au coverage increases the population of defects increases which favors formation of the (1x3) channels and thus the dominance of the (1x3) diffraction pattern for thicker Au films. The defects resulting from the lattice strain explain the coverage dependence and temperature independence for the half-order splitting observed for the Au films.

For the Pt films the break down in the two-dimensional order (smoothness) occurs due to agglomeration, and some degree of dissolution, of the films as they are annealed to higher temperatures. The continuous splitting observed as a function of temperature results from an increase in the two-dimensional disorder as the temperature is raised. As temperature increases the relative population of (1x3) regions grows relative to (1x2) regions. As agglomeration continues and disorder grows the (1x3) becomes the majority species and dominates the diffraction pattern.

There exist two other distinguishing characteristics which support the different growth mechanisms proposed for the Au-Pd and Pt-Pd systems. The first is the quality of the LEED patterns observed at higher coverages. The second is the observed decrease in the overlayer Auger signal relative to the substrate as the films are annealed to high temperatures, in conjunction with the quality of the LEED patterns after annealing to these temperatures. An indication of the defective nature of the Au films at higher coverages is reflected in the decreased

integral-order and fractional-order LEED beams as the film thickness increases as was shown previously (4). After deposition of 5 to 6 monolayers of Au followed by heating to induce the reconstruction, the fractional order beams are barely visible over the background. For the Pt films however, relatively sharp beams are obtainable even for films which are 15 layers thick, and reflect a less defective film resulting from the small lattice mismatch for Pt and Pd system. As the Au and Pt films are heated to high temperatures all superstructures are lost and a (1x1) diffraction pattern is obtained. A drastic reduction in the Au and Pt Auger signals also occurs simultaneously with the loss of the superstructures. In the case of the Au films (4), we speculated that this decrease in the Au intensity and loss of the fractional-order beams was due to dissolution of the film into the Pd substrate. For the Pt it is thought that the loss of the fractional-order beams and substantial decrease in the Pt Auger signal results from agglomeration of the Pt films at higher temperatures. The increased tendency for Au rather than Pt to alloy with Pd is supported by calculations for the heats of formation of 50:50 bulk alloys given by Miedema (69) for which he lists a value of 0 kJ/mole for the Au-Pd system and +3 kJ/mole for the Pt-Pd system. The alloying of Au with Pd is also suggested by the coverage independence observed for the onset of the decrease in the Au/Pd Auger ratio (4) as discussed previously. Evidence of Au-Pd alloy formation and Pt agglomeration is also suggested by the quality of the LEED patterns following annealing to temperatures high enough to substantially reduce the overlayer Auger signals. For Au (4), annealing to these temperatures

results in a very disordered LEED pattern. The integral order spot intensities are substantially less than those for the clean Pd substrate. The high disorder observed in the LEED pattern following annealing of the Au films may be evidence of alloying. If alloying occurs, one would think that this would induce disorder in the Pd surface and result in a poor diffraction pattern with a high background intensity. This is what is observed for the Au-Pd system (4). However, in the case of Pt on Pd the integral order beam intensity following heating and loss of the fractional-order spots is about as strong as that for the clean Pd surface. This probably results from the agglomeration of the Pt at high temperatures which opens up bare patches of the clean Pd surface and thus restores a rather strong (1x1) diffraction pattern. Therefore, at high temperatures we believe that dissolution occurs for the Au films while agglomeration results for the Pt films.

We believe the main differences in the Au-Pd and Pt-Pd systems which leads to the different growth mechanisms observed, and thus the difference in the (1x2) to (1x3) transitions, lies in the free energy differences for each respective metal pair, and in the different strain energies involved at the interface resulting from the dissimilar lattice mismatches for these two systems.

V. CONCLUSIONS

We have conducted a detailed study of the growth and reconstruction of Pt films on Pd(110). We find that for deposition at room temperature or below a pseudo-Frank-van der Merwe growth mode is followed. Annealing films deposited at room temperature results in the formation of a (1x3) superstructure for films greater than 2 layers deep. The (1x3) is found to develop by the continuous splitting of a broad half-order spot as the temperature increases. This transition to the (1x3) results from a break down in the two-dimensional order (smoothness) of the Pt films as the temperature is raised. The (1x3) channels are thought to be favored by the disordering of the film and thus become the majority species as the temperature increases resulting in the dominance of the (1x3) structure. The transition to the (1x3) therefore results from a morphological change in the film resulting from a thermodynamic drive toward three-dimensional growth.

We have also studied the growth of the Pt films under a variety of deposition conditions. We find that for deposition of 3 layers of Pt at 130 K a (1x2) structure can be stabilized. Increasing the deposition temperature up to 200 K while keeping the coverage constant results in a steady increase in the FWHM of the half-order spot. Increasing the deposition temperature to 225 K for the 3 layer film results in a partial splitting of the half order spot following annealing. Finally by a deposition temperature of 300 K the half-order spot splits fully into the (1x3) after annealing. We believe that the temperature dependence we

find for the transition of the Pt (1x2) and (1x3) structures results from a combination of thermodynamic and kinetic effects which control the film growth at the Pt-Pd interface. Our results are most consistent with a model in which low temperature deposition kinetically traps a higher quality layer-by-layer growth into the film resulting in a higher long range ordering of the (1x2) reconstruction, and thus a stabilization of the (1x2) for low temperature deposition. As deposition temperature increases so does the mobility of the Pt adatoms and the thermodynamics of the system induces a trend toward the microscopic two-dimensional disordering of the film. The increase in the two-dimensional disorder is enhanced at higher deposition temperatures resulting in the transition to the (1x3). The deposition temperature dependence for the 3 layer films we find is not due to H contamination resulting from adsorption from the background. We also do not believe it results from an order-disorder transition of the Pd(110) surface which is thought to occur at temperatures around 230 K (65). Instead we believe that the temperature dependence we find for the transition of the Pt (1x2) to the (1x3) structure results from a combination of thermodynamic and kinetic effects which control the film growth at the Pt-Pd interface.

We believe that the (1x2) and (1x3) structures which we observe for the Pt films are a result of true missing row reconstructions. This has been proven by the complete reversibility of these structures with the (1x1) upon adsorption and desorption of CO. We have also observed these same reconstructions for the Au on Pd(110) system (4). However, the transformation of the (1x2) to the (1x3) structure by the continuous

splitting of the half-order spot was found to be only dependent on the film thickness for the Au on Pd(110) system. This was explained by the formation of defects in the film for coverages in excess of two layers which induced a similar reduction in the two-dimensional order (smoothness) of the Au films. No temperature dependence is found for the (1x2) to (1x3) transition of the Au films as was found for the Pt films. This occurs because the formation of the defects which induce the transition in the Au films are caused by the interfacial strain from the lattice mismatch and their formation are not kinetically controlled by the substrate temperature.

The differences which we have found in the results for growth and reconstruction of the Pt and Au films on Pd(110) can be traced to simple factors which are known to affect film growth processes. We use criteria proposed by Bauer (57) to explain the different results observed for the Pt and Au films on Pd(110). We propose for both the Pt-Pd and Au-Pd systems that the transition of the (1x2) to (1x3) results from a slow break down of the two-dimensional order (smoothness) of the films which favors the formation of (1x3) channels. We believe the main differences in the Au-Pd and Pt-Pd systems which leads to the different growth mechanisms observed, and thus the difference in the (1x2) to (1x3) transitions, lies in the surface free energy differences for each respective metal pair, and in the different strain energies at the interface resulting from the dissimilar lattice mismatches for these two systems.

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CONCLUSIONS

In this dissertation, we investigate the growth, structure, and thermal stability of various vapor-deposited, ultra-thin film systems: Rh on Ag(100), Au on Pd(110), and Pt on Pd(110). The main factors which discriminate between the different film-substrate combinations presented here are: (1) the different substrate morphologies, (100) vs. (110); (2) the differences in surface free energies between an overlayer and the substrate; (3) the degree of lattice mismatch for a particular system; and (4) the extent of miscibility of the two metals. By varying the overlayer-substrate properties we have gained some insight into how these properties are related to the growth and resulting structure of the three systems. The main conclusions which can be drawn are summarized below:

(a) The difference in surface morphology, Ag(100) vs. Pd(110), does not contribute significantly to the differences found between the three systems studied. The substrate surface crystallography only promotes the continuation of its crystal structure for the growing films.

(b) The surface free energy of the film and substrate metals, as proposed by Bauer, governs the equilibrium structure of thin films (27). Traditionally for a system such as Rh on Ag(100), where the free energy of the film is larger than that of the substrate (28,29) and the interfacial energy is probably small, the film should grow three-dimensionally to expose a large area of the substrate and thus keep the surface energy at a minimum. However, we have shown that if the mobility of the substrate atoms is sufficient to allow diffusion which results in

a lowering of the surface energy, agglomeration need not be invoked.

For the cases of Au and Pt on Pd(110), the initial stages of the film growth are consistent with the differences in free energies for these overlayer-substrate combinations (28,29). Au grows layer-by-layer on Pd(110) for the first few layers, whereas Pt grows more three-dimensionally under equilibrium conditions. Substrate diffusion in the case of Au on Pd would not be thermodynamically favorable, although it may be for Pt on Pd. Presumably for Pt on Pd(110), the substrate atom mobility is not significantly faster than the Pt atom mobility so that agglomeration rather than substrate diffusion occurs for this system.

(c) The degree of lattice mismatch for a metal film system substantially influences the energetics of interface formation by means of strain energy contributions. For the systems studied, Rh/Ag(100), Au/Pd(110), and Pt/Pd(110), the degree of lattice mismatches are 7.1%, 4.8%, and 0.8%, respectively (30). In the case of Rh on Ag(100), the high lattice mismatch presumably results in the formation of a high defect density creating a porous film through which Ag can diffuse. For Au on Pd(110), the Au grows epitaxially for the first two layers, after which the strain energy from the 4.8% lattice mismatch becomes significant and layer growth breaks down and becomes more three-dimensional. For Pt films on Pd(110) the lattice mismatch is so small that Pt films up to 15-20 layers thick can be stabilized with little noticeable contributions from lattice strain (i.e., degradation of integral-order LEED beam intensity and FWHM).

(d) The miscibility of the film and substrate metals is usually

associated with the thermal stability of the film in relation to the competing processes of dissolution and agglomeration. For Rh on Ag(100), as the temperature is raised and equilibrium is approached, Ag diffusion through the Rh film occurs. Due to the limited miscibility of Rh and Ag (31) and the high Ag atom mobility, a Ag/Rh/Ag sandwich complex forms, the layers being relatively pure. For Au on Pd(110), dissolution at the interface occurs as the system is heated, consistent with the bulk Au-Pd phase diagram (32) which exhibits a continuous series of solid solutions. For Pt on Pd(110), the films agglomerate following annealing. Although alloying is favorable for the Pt-Pd bulk system (33,34), presumably film agglomeration is activated at a lower temperature than dissolution resulting in the clustering of the Pt films.

(e) For Rh on Ag(100) the differences in surface free energies, the high mobility of the Ag atoms, the slightly defective nature of the film, and the immiscibility of the two metals govern the equilibrium structure of this system and result in the Ag/Rh/Ag sandwich formation. Sandwich formation is not observed for Au or Pt on Pd(110). For the case of Au this is due to unfavorable thermodynamics, and for Pt there is presumably a lower activation barrier to agglomeration of the film relative to Pd diffusion or to Pt-Pd alloy formation. In comparing the Au/Pd(110) and Pt/Pd(110) systems we believe the main differences in these systems which leads to the different growth mechanisms observed, lies in the surface free energy differences for each respective metal pair, and in the

different strain energies involved at the interface resulting from the dissimilar lattice mismatches for these two systems.

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APPENDIX A:

Ir FILMS GROWN ON Pd(110)

I. INTRODUCTION

The growth and structure of ultra-thin metal films (1 to 10 monolayer regime) is an on going topic of research in our laboratories. We have been particularly interested in the growth of metal films whose bulk surfaces are known to reconstruct (1-3), and how the factors which control film growth can affect the bulk-like reconstructions of these films. The (100) and (110) low index faces of bulk Au, Pt, and Ir are known to reconstruct, i.e., their surfaces rearrange to form an atomically different two-dimensional periodicity than that of the bulk crystal (4, and Ref. therein). Few reports exist on the study of Au, Pt, or Ir films grown on an fcc (110) substrate. To the best of our knowledge only Fenter and Gustafsson have worked with films on an fcc (110) surface, the system being Au on Ag(110) (5). We therefore have recently concentrated our efforts on the study of metal films on an fcc (110) substrate, Pd(110) (2-3). The clean (110) surface of bulk Pd is stable against reconstruction (6,7).

The (110) faces of Au, Pt, and Ir are known to exhibit (1xn) "missing row" reconstructions (4,8-10). We have recently reported results on the growth and reconstructions of Au and Pt films on Pd(110) (2-3). For these systems we find evidence for both (1x2) and (1x3) reconstructions, their formation depending upon film thickness and deposition temperature. As a continuation of our study of the reconstruction of metal films, we have investigated the growth and reconstruction of Ir films on Pd(110). By studying the growth of Au, Pt,

and Ir films we have a means of comparing how differing growth conditions can effect the bulk-like reconstructions for these systems.

II. EXPERIMENTAL PROCEDURES

The experiments are carried out in an ultrahigh vacuum chamber equipped with a shuttered Ir evaporation source, a cylindrical mirror analyzer for Auger electron spectroscopy (AES), and optics for low-energy electron diffraction (LEED). Base pressures are below 2×10^{-10} Torr.

The Pd crystal which has been oriented to within $\pm 1^\circ$ of the (110) plane is the same as that used previously (2,3). The crystal is cleaned by repeated cycles of argon-ion bombardment (1 keV, $1.5 \mu\text{A}/\text{cm}^2$) at 300 K, followed by cycling in oxygen to remove carbon and heating to 1100 K to desorb residual oxygen. The sample is mounted by spotwelds to two Ta support rods which in turn are connected via copper braids to current feedthroughs in a liquid nitrogen reservoir. This configuration allows the sample temperature to be varied from 130 K up to 1100 K by resistive heating of the crystal. The crystal temperature is monitored by a W-5% Re/W-26% Re thermocouple spotwelded to the back of the sample.

Ir is deposited on the sample surface from a resistively-heated tungsten filament wrapped with 0.25mm diameter Ir wire (99.9%), following the design of DeCooman and Vook (11). We have modified the filament assembly by reducing the number of tungsten wires from three (as used by DeCooman and Vook (11)) to two. This modification eliminates the center gap used in the three wire assembly, but increases the resistance of the entire filament and thus requires less power to achieve the higher filament temperatures needed to evaporate Ir. The Ir source is enclosed in a double-walled, liquid-nitrogen-cooled shroud with a 1.5 cm orifice

to allow Ir vapor to escape toward the sample. After thorough outgassing of the filament, the pressure of the system during evaporations is on the order of 1×10^{-9} Torr. No impurities can be detected by AES after deposition of the films. Also using AES, the Ir distribution across the sample surface is found to be uniform to within $\pm 5\%$. The Ir is removed by argon-ion bombardment after each experiment. The conditions of bombardment are 1 keV, ca. $1.5 \mu\text{A}/\text{cm}^2$, at 300 K.

The Ir films are deposited by exposing the Pd crystal, held at the desired deposition temperature, to the Ir vapor flux. The resultant film thickness is determined by AES. After deposition, the sample is slowly heated to a desired temperature, held for 20 seconds at constant temperature to allow equilibration, and then quenched below 200 K where the LEED pattern is observed.

III. EXPERIMENTAL RESULTS

We begin our investigation of Ir films on Pd(110) by monitoring the growth of the $\text{Ir}_{54}(\text{NVV})$ and decay of the $\text{Pd}_{330}(\text{MNN})$ Auger transitions as a function of deposition time at 300 K. These results are plotted in Fig. 1 as the peak-to-peak heights of the derivative spectra for Ir and Pd, and as the Ir to Pd Auger intensity ratio. As was found for Au and Pt films on Pd(110) (2-3), these plots are rather smooth and continuous. No information as to the growth mode or coverage calibration of the films can be obtained from these results. We use the AES results from our Au on Pd(110) study (2) together with a comparison of intensity cross-sections for the $\text{Au}_{69}(\text{NVV})$ and $\text{Ir}_{54}(\text{NVV})$ Auger transitions obtained from handbook spectra (12) to calibrate our Ir coverages. In Fig. 1 the first monolayer corresponds to a 40 to 50 second evaporation time. Subsequent layers are based on a multiple of this time period assuming a constant evaporation rate.

We use LEED to follow the evolution of the two-dimensional order of the Ir films as a function of coverage and temperature. Similar to Au and Pt, the clean Ir surface has been shown to reconstruct, the activation barrier to reconstruction being reached at temperatures of 570 to 670 K (13). We deposit our Ir films at low temperatures, 130 K, and anneal the films slowly while monitoring the LEED pattern. The appearance of any additional fractional order spots along the [001] direction would indicate reconstruction of the Ir films.

Following deposition of 2 to 5 monolayers of Ir, and annealing to

Figure 1. Variation of the Ir₅₄(NVV) and Pd₃₃₀(MNN) Auger signals versus deposition time following deposition at 300 K
 a) Plotted as the peak-to-peak amplitude of the derivative spectra.
 b) Plotted as the ratio of the peak-to-peak amplitudes of the Ir and Pd derivative spectra.

temperatures around 500-600 K, heavy streaking along the [001] direction is observed. Annealing to higher temperatures results in the return of the (1x1) pattern. Distinct fractional-order spots are never observed even following longer annealing times or deposition of thicker Ir films. AES results indicate that following annealing to temperatures around 600 K, significant loss of the Ir Auger signal has occurred. This is demonstrated in Fig. 2 where the Ir/Pd Auger ratio is plotted as a function of annealing temperature for three different Ir coverages. It is evident from Fig. 2 that an initial decrease in the Ir/Pd Auger ratio occurs at about 600 K for all three Ir films shown. The loss of Ir at 600 K must be responsible for the inability to stabilize the Ir film reconstruction.

Figure 2. Variation of the $\text{Ir}_{54}(\text{NVV})$ to $\text{Pd}_{330}(\text{MNN})$ Auger peak ratio versus annealing temperature for a series of Ir films deposited at 130 K

IV. DISCUSSION

In our investigations of Au and Pt films on Pd(110) (2-3) we were able to stabilize (1x2) and (1x3) reconstructions of the metal overlayers. However, for Ir we do not observe any well defined fractional-order LEED spots which would be indicative of a well developed reconstruction of the films. For Ir we only observe heavy streaking along the [001] direction following annealing of the films to 600 K. In the case of the reconstruction of the bulk Au and Pt (110) surfaces the (1x2) reconstructions are found to develop at temperatures of 350 K (14) and 315 K (15), respectively. For the bulk Ir(110) surface the (1x2) reconstruction was found to develop at temperatures of 570 to 670 K (13).

Our Auger results show that following annealing of the Ir films to temperatures high enough to activate the reconstruction results in a significant loss of the Ir Auger signal. Presumably the Ir films are not stable at these high temperatures due to dissolution and/or agglomeration of the films. Ir and Pd are partially miscible as shown by the Ir-Pd bulk phase diagram (16). Agglomeration of the Ir, however, cannot be precluded. The surface free energy of Ir, 3.23 J/m^2 (17), is larger than that for Pd, 2.04 J/m^2 (17), which would favor clustering if dissolution was not significant at the same temperature. Agglomeration could also explain the loss of the Ir Auger signal. However, a simple depth profile of an Ir film annealed to a temperature high enough to result in loss of the Ir signal favors the dissolution argument. The results of the depth profile are shown in Fig. 3. Here an Ir film, 5 layers thick, was

Figure 3. Depth profile of a 5 layer Ir film, deposited at 300 K and annealed to 790 K for 20 seconds

The conditions of argon-ion bombardment are 20 mA of filament emission current at an argon pressure of 2×10^{-6} Torr. The beam was defocussed to cover an area of $\approx 1 \text{ cm}^2$, and resulted in an ion-current at the sample of $\approx 70 \text{ nA}$.

deposited at room temperature and then annealed to 790 K for 20 seconds. The film was then slowly ion-etched while following the $\text{Ir}_{54}(\text{NVV})$ and $\text{Pd}_{330}(\text{MNN})$ Auger transitions. If agglomeration was occurring one would expect a continuous drop in the Ir/Pd Auger ratio with sputtering time as the Ir clusters are slowly etched away. However, we observe an increase in the Ir/Pd Auger ratio with sputtering time indicating an increase in the Ir concentration relative to Pd. It is well known for binary alloys, that surface enrichment of one of the components may occur due to preferential segregation. In fact, surface segregation of Pd is predicted for the Ir-Pd alloy system (18). A depth profile of an Ir-Pd alloy with segregated Pd would be very similar to that shown in Fig. 3, where the segregated Pd is removed first thus increasing the Ir concentration relative to Pd as the depth profile proceeds. We therefore believe that dissolution of the Ir films into the Pd best describes our experimental results and is the cause of the decrease in the Ir Auger signal at high temperatures.

V. CONCLUSIONS

Our results indicate that the temperature needed to activate the Ir reconstruction, 570-670 K (13), is higher than the activation barrier to dissolution of the Ir into the Pd substrate. The instability of the films at these temperatures inhibits the Ir reconstruction. For Au and Pt films on Pd(110) the lower activation barrier for reconstruction (14,15) allows the reconstruction to develop before contributions from dissolution and/or agglomeration become significant.

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APPENDIX B:

ISOTOPE EFFECT IN WATER DESORPTION

FROM Ru(001)

ISOTOPE EFFECT IN WATER DESORPTION
FROM Ru(001)

P. J. Schmitz¹, J. A. Polta², S. -L. Chang³, and P. A. Thiel¹

¹Department of Chemistry and Ames Laboratory
Iowa State University
Ames, Iowa 50011

²Henkel Research Corporation
2330 Circadian Way
Santa Rosa, California 95407

³Department of Physics
Montana State University
Bozeman, Montana 59717

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ABSTRACT

It is well-established that three features are resolved in the thermal desorption spectra of H_2O from clean $\text{Ru}(001)$: one at low temperature due to desorption from ice multilayers, and two at higher temperatures due to desorption from a chemisorbed bilayer. However, we find that for D_2O the highest-temperature state is strongly suppressed. By varying the heating rate during H_2O desorption, we obtain evidence that the highest temperature state can be formed by *conversion* from the intermediate state. Conversion is much slower for D_2O than for H_2O , so that direct desorption is kinetically favored over conversion and the high temperature state is suppressed for D_2O . The rate of conversion is about 3 to 8 times slower for D_2O than for H_2O , which is consistent with a model in which the rate-determining step for conversion is rotation of one or more water molecules within a hydrogen bonded cluster. This work provides the first evidence for an isotope effect in thermal desorption of water. An important ramification is that adsorbed D_2O is *not* always interchangeable with H_2O for chemical studies of isotopic mixing or for spectroscopic studies of vibrational frequency shifts, as is commonly assumed.

I. INTRODUCTION

Thermal desorption spectra of H_2O from $\text{Ru}(001)$ were first reported by Madey and Yates in 1977 (1). They observed three features which they attributed to *independent* desorption from a chemisorbed layer of H_2O in direct contact with the metal, a second layer above the first, and ice-like multilayers (1). These spectra have been subsequently reproduced in their essential features by several groups (2-5). The three desorption features originally reported by Madey and Yates (1) are represented in Fig. 1(A) and are labelled A_1 , A_2 , and C, respectively.

Additional data from other experimental techniques later showed that hydrogen bonding between adsorbed water molecules is very important in determining the properties of the chemisorbed layer (1-4,6,7). This led Doering and Madey to reinterpret the A_1 and A_2 states as arising from water molecules at or near the ruthenium surface, with different stabilities (3). In 1984, Thiel, DePaola and Hoffmann measured the vibrational spectra of the hydrogen-bonded water clusters associated with each of the desorption states (4). This large body of experimental data provides a basis for interpretation of our present results, in which an isotope effect is observed in thermal desorption spectra of H_2O and D_2O from $\text{Ru}(001)$. Our data further indicate that a structural conversion can take place during the thermal ramp. Rotational motion among water molecules may be involved in the structural transition, consistent with a slower rate of conversion for D_2O than for H_2O .

Figure 1. Thermal desorption spectra of water from Ru (001), following exposure at 90 K. The heating rate is 10 K/s.
 A) Desorption of H₂O (18 amu) following exposure to H₂O.
 B) Desorption of D₂O (20 amu) following exposure to D₂O. The inset shows the simultaneous desorption yields of D₂O, HDO, and H₂O (20, 19, 18 amu, respectively) during a typical experiment; the initial coverage is 1.1 monolayers for the inset.

II. EXPERIMENTAL PROCEDURES

A complete description of the experimental arrangements are found elsewhere (5). In short, the experiments are done in an ultrahigh vacuum chamber (base pressures of $\leq 2 \times 10^{-10}$ Torr) equipped with a single-pass CMA, ion gun, effusive beam doser, and computer-interfaced mass spectrometer. The H_2O and D_2O are repeatedly freeze-thawed on the vacuum line to remove dissolved atmospheric gases. The Ru sample is exposed to H_2O by backfilling the chamber, and it is exposed to D_2O via the effusive beam doser. The purity of the D_2O is ~70%, with 10% HDO and 20% H_2O . The hydrogen impurity appears to result from exchange between the D_2O and OH groups on the glass capillary array at the end of the doser. We cannot obtain more than 70% isotopic purity of the D_2O even after extensive conditioning of the doser and gas manifold.

We define a coverage of one monolayer, $\theta = 1$, as one adsorbed molecule per Ru surface atom. Previous studies (2-4,6,7) indicate that a hydrogen bonded network of water molecules, two layers deep, covers the surface before the ice multilayer is populated. When this bilayer is filled, the absolute coverage is 0.67 monolayers (2-4,6,7). The absolute coverages for water given in Fig. 1(A) are based upon this fact.

The coverage calibration for D_2O is achieved by comparing the time-integrated peak areas with those of H_2O . Since the isotopic purity of D_2O is only 70%, masses 20, 19, and 18 are monitored simultaneously in all experiments and the total integrated peak areas are found by adding the areas of all three isotopes. The coverage indicated for D_2O in Figs.

1(B) and 2 are the total coverages obtained in this way.

The heating rates used in the experiments are linear to within $\pm 12\%$ between 120 and 250 K.

III. EXPERIMENTAL RESULTS

In Fig. 1(A) we show a series of thermal desorption spectra of H_2O . The exposure of H_2O increases from the bottom to the top curve, as indicated. At low coverages water desorbs in the A_1 state (centered at ~ 215 K) and the A_2 state (at 200 K). These peak positions shift to 220 and 185 K, respectively, as coverage increases. The bilayer is filled after an exposure of 2.5 L, at which point $\theta = 0.67$ (2-4,6,7); at higher exposures the ice multilayer state (labelled C) appears at 165 K.

In Fig. 1(B), we show thermal desorption spectra following exposure of D_2O to Ru(001). The A_1 state is strongly suppressed for D_2O . However, the A_2 state and ice multilayer states appear as for H_2O , and at the same peak temperatures within ± 2 K (which is within our experimental uncertainty). As shown in Fig. 2, the suppression of the A_1 state in D_2O desorption is observed over a wide range of heating rates and initial coverages.

We have considered, and ruled out, three experimental artifacts which could possibly account for the suppression of the A_1 state in D_2O desorption: isotopic impurity, sample contamination, and differences in angular distribution between the isotopes. In the first case, it might be that the A_1 state is dominated by the other isotopes present in the D_2O . (As discussed in section II, the D_2O is approximately 70% D_2O , 10% HDO , and 20% H_2O in composition.) In experiments where mass 18 (H_2O) and 19 (HDO) are monitored at the same time as mass 20 (D_2O) following nominal exposure to D_2O , however, the desorption peak shapes of all

Figure 2. Desorption of D_2O and H_2O at different heating rates (β), and different coverages. The curves are labelled with the values of β in K/s. For each value of β , the data are expanded along the y-axis by the factor indicated as y . For example, the spectra taken at 2 K/s are expanded vertically by a factor of four relative to the spectra taken at $\beta = 25$ K/s.

isotopes are identical. One such experiment is shown for illustration in the inset of Fig. 1(B). A second explanation which we have considered is that the sample is contaminated during the D_2O experiments, leading to the suppression of the A_1 state. However, we reject this possibility on the basis that these data are completely reproducible over several months and after different combinations of sample pre-treatment, including ion-bombardment, cleaning with oxygen, and annealing to 1600 K. Sample contamination is not detectable with Auger electron spectroscopy. Furthermore, the H_2O thermal desorption spectra (where the A_1 state is not suppressed) can be reproduced *interchangeably* with the D_2O spectra. Sample contamination, therefore, is *not* a feasible explanation for the differences between our H_2O and D_2O TDS data.

The third explanation could be that the spacial distribution of desorbing H_2O and D_2O are much different in the A_1 state. If H_2O were more closely confined to trajectories along the surface normal than D_2O during A_1 desorption, while angular distributions of the A_2 and C states were insensitive to isotopic substitution, then our mass spectrometer (in direct line-of-sight with the sample and about 3' removed) could be more sensitive to H_2O than D_2O in the A_1 state. However, the shapes of the TD spectra for H_2O and D_2O are not sensitive to changes in the angle between the sample and the mass spectrometer, and so we reject this possibility as well.

Further information is provided by experiments in which the heating rate is varied. Fig. 2 demonstrates that a slow heating rate can enhance the intensity of the A_1 state relative to the A_2 state, presumably by $A_2 \rightarrow$

A_1 conversion, whereas desorption from the A_2 state is enhanced by faster heating rates. The sets of spectra shown in Fig. 2 illustrate this effect for three different H_2O coverages. At the slowest heating rate ($\beta = 2$ K/s), the A_2 state is merely a small shoulder on the A_1 state, but when the heating rate is increased ($\beta = 25$ K/s) the two peaks are of roughly equal intensity. This enhancement of the A_1 state at slower heating rates is not as dramatic at higher coverages, especially when the ice multilayer is populated. For D_2O , the A_1 state is entirely absent for heating rates above 4 K/s; it is visible only as a small shoulder at lower values of β .

Previous work (4) also reported that the effect of slow annealing is to increase the number of molecules which desorb in the A_1 state, although in that study changes in the absolute A_1 peak intensity due to fluctuations in pumping speed between successive adsorption-desorption experiments could not be completely ruled out. In the present experiments, the influence of pumping speed is irrelevant to our conclusions so long as the A_1 and A_2 states are separable, since we only compare *relative* intensities during a given desorption experiment.

In Fig. 2, the A_1 state is observed at 205-210 K when D_2O desorbs at slow heating rates. This is 5-10 K lower than the A_1 peak temperature of H_2O under comparable conditions of β and *total* coverage. This difference in peak temperatures for H_2O and D_2O is probably due to the difference in coverage *within* the A_1 state for the two cases. The A_1 peak temperature increases with coverage for H_2O (cf. Fig.1(A)), and the extremely low coverage in the A_1 state for D_2O is therefore compatible with its low

peak temperature. In short, there is probably no difference between the kinetics of desorption in the A_1 state for H_2O and D_2O .

In Figs. 1 and 2, there is always a small desorption feature at 165 K, even at very low coverages, where it cannot be explained as desorption from the ice multilayer. This has been observed previously by Doering and Madey (3), who suggest that it is due to desorption from the back of the crystal. An alternative explanation is that it is due to desorption of water monomers (8), whereas desorption from the A_1 , A_2 , and C states is limited by rates of decomposition of hydrogen-bonded aggregates (3). The relatively small size of this feature, even at low water coverages, indicates that such monomers would be in the minority, consistent with previous work (2-4).

IV. DISCUSSION

Any model for the A_2 and A_1 desorption states must be compatible with the observations which we summarize here:

(1) Desorption from the A_1 state is favored by slow heating rates; desorption from the A_2 state is enhanced by rapid heating rates. We interpret this to mean that conversion from the A_2 to A_1 state can occur, and the process of conversion is kinetically competitive with desorption from the A_2 state.

(2) Conversion occurs more slowly for D_2O than H_2O , relative to A_2 desorption, which we interpret as a kinetic isotope effect.

Our data support the following model: As temperature increases during a thermal desorption experiment, activated structural rearrangement of some molecules can occur. These molecules would otherwise desorb in the A_2 state, but if they can rearrange into the more stable configuration, they desorb in the A_1 state. We observe that rearrangement is faster, relative to desorption, for H_2O than for D_2O (see Fig. 1). This means that a kinetic isotope effect determines the relative rates of desorption and structural transition.

There are essentially two types of isotope effects which can influence reaction kinetics: the normal isotope effect, and the inverse isotope effect. The former is due mainly to higher zero-point vibrational energies for bonds in the reactants with lighter isotopes; such bonds break more rapidly than those with heavier isotopes (9). This

is observed frequently in organic chemistry, and had been observed also in surface reactions, such as the decomposition of methanol on nickel (10). The inverse isotope effect is poorly understood, but presumably occurs because differences in zero-point energies in the transition state outweigh the differences in the ground state (9).

We find that the rate of $A_2 \rightarrow A_1$ conversion, relative to the rate of A_2 desorption, is slower for D_2O than for H_2O . This could be either because the absolute rate of desorption in the A_2 state is faster for D_2O than for H_2O (inverse isotope effect), or because the absolute rate of $A_2 \rightarrow A_1$ structural conversion is slower for D_2O than for H_2O (normal isotope effect). However, the peak shape and peak temperature of the A_2 state is the same (within experimental uncertainty, about ± 2 K), for both H_2O and D_2O (see Fig. 1). This indicates that the kinetics of A_2 desorption are the same for the two isotopes. Therefore, an inverse isotope effect does not appear to be a plausible explanation.

For the normal isotope effect, we must conclude that the absolute rate of $A_2 \rightarrow A_1$ conversion is slower for D_2O than for H_2O . Simple modelling enables us to roughly estimate the magnitude of the isotope effect in this system. We assume that there are three independent kinetic processes which can occur, illustrated in Fig. 3. We further assume simple first-order kinetics for each step, with Arrhenius-type rate constants. The three processes can then be described by three rate equations:

(1) Desorption from the A_2 state:

Figure 3. Schematic depiction of surface processes considered in model

$$R_{A_2 des} = \theta_{A_2} \nu_{A_2 des} \exp\left(\frac{-E_{A_2 des}}{kT}\right),$$

(2) Conversion from A_2 into A_1 :

$$R_{con} = \theta_{A_2} \nu_{con} \exp\left(\frac{-E_{con}}{kT}\right),$$

(3) Desorption from the A_1 state:

$$R_{A_1 des} = \theta_{A_1} \nu_{A_1 des} \exp\left(\frac{-E_{A_1 des}}{kT}\right).$$

In these equations, R is a rate of desorption or conversion in monolayers per second, θ_x is the absolute coverage of state x in monolayers, ν is a pre-exponential factor for desorption or conversion, E is an activation barrier for desorption or conversion, k is Boltzmann's constant, and T is the sample temperature in K. We are primarily interested in the relative rates of desorption and conversion from the A_2 state:

$$\frac{R_{con}}{R_{A_2 des}} = \frac{\nu_{con}}{\nu_{A_2 des}} \exp\left[\frac{-(E_{con} - E_{A_2 des})}{kT}\right].$$

This ratio determines the relative intensities of the A_1 and A_2 desorption features, and the way in which these relative intensities change with heating rate. The data available for comparison are shown in Fig. 2, and typical results from the modelling are shown in Fig. 4. A

Figure 4. Kinetic modelling of A_2 and A_1 states, as described in text. The initial coverage is arbitrarily set at 1, and the following parameters are held constant: $E_{A_2 \text{ des}} = 10$ kcal/mol, $E_{A_1 \text{ des}} = 13$ kcal/mol, and $\nu_{A_2 \text{ des}} = 10^{13} \text{ s}^{-1}$. For H_2O , $E_{\text{con}} = 7.0$ kcal/mol and $\nu_{\text{con}} = 1.5 \times 10^9 \text{ s}^{-1}$. For D_2O , $E_{\text{con}} = 7.5$ kcal/mol and $\nu_{\text{con}} = 1.5 \times 10^9 \text{ s}^{-1}$. The model curves should be compared with the data of Fig. 2.

good qualitative fit to the data is quite sensitive to the values of the two relative parameters ν' and E' , where

$$\nu' = \frac{\nu_{con}}{\nu_{A_2des}}$$

and

$$E' = E_{con} - E_{A_2des}.$$

The latter term carries the temperature-dependence (and therefore the heating-rate dependence) of the system, i.e. it is the term which controls the variation of the $A_2:A_1$ intensity ratio with heating rate. Note that the $A_2:A_1$ intensity ratio is not sensitive to the *absolute* values of the desorption rate parameters; this ratio is only sensitive to the *relative* parameters ν' and E' , and to the assumption that desorption and conversion from the A_2 state are both first-order processes. For the purposes of modelling the $A_2:A_1$ peak height ratio, we use values for the desorption rate parameters which are chosen rather arbitrarily.

The isotope effect we are interested in is R^* , where

$$R^* = \frac{R_{con}(H_2O)}{R_{con}(D_2O)}.$$

If we assume (as the data suggest) that

$$R_{A_2 des}(H_2O) = R_{A_2 des}(D_2O) ,$$

then

$$R^* = \frac{R'(H_2O)}{R'(D_2O)} = \frac{\nu'(H_2O)}{\nu'(D_2O)} \exp \left\{ \frac{-[E'(H_2O) - E'(D_2O)]}{kT} \right\} .$$

In Fig. 5 we show the experimental ratio of $A_2:A_1$ peak heights as a function of heating rate for both H_2O and D_2O , at $\theta = 0.1$ to 0.3 . In the same form, we also show the results from the modelling. For H_2O , the data can be fit with a range of parameters from $E' = -4$ to -2 kcal/mol and $\nu' = 7 \times 10^{-6}$ to 3.6×10^{-3} . For D_2O , the data are described by a range of E' from -3.5 to -1.5 kcal/mol and $\nu' = 7 \times 10^{-6}$ to 3.6×10^{-3} . For any chosen value of E' within the ranges stated, the corresponding value of ν' cannot be varied by more than ca. $\pm 10\%$, i.e., for a given isotope the *rate constant* for conversion, relative to that for desorption, is fixed quite closely by the data of Fig. 5. We calculate the following values for the relative rate constants at 150 K:

$$\nu'(H_2O) \exp \left[\frac{-E'(H_2O)}{kT} \right] = 2.8 \text{ to } 4.3 .$$

$$\nu'(D_2O) \exp \left[\frac{-E'(D_2O)}{kT} \right] = 0.53 \text{ to } 0.82 .$$

Therefore,

Figure 5. Relative peak heights of A_2 and A_1 desorption states as a function of heating rate, β

Results are shown for both D_2O and H_2O . The symbols represent experimental data and the solid lines show results from the modelling described in the text, using these parameters: for H_2O , $E' = -3.0$ kcal/mol and $\nu' = 1.5 \times 10^{-4}$; for D_2O , $E' = -2.5$ kcal/mol and $\nu' = 1.5 \times 10^{-4}$. These are the same parameters used to generate Fig. 4.

$$R^*=3.4-8.1$$

The average value of R^* is 5.8. The range of R^* is not sensitive to T between 150 and 180 K, where conversion actually occurs.

Normal isotope effects are usually due to breaking of bonds which involve hydrogen, such as O-H bonds. However, less than 5% of a monolayer of water dissociates on Ru(001) (1-3), so that rupture of the O-H bond cannot explain our data. Rather, we posit that the isotope effect is related to structural changes which take place in the chemisorbed layer during the thermal ramp. Doering and Madey first proposed that the A_2 and A_1 desorption states correspond to water desorption from large and small hydrogen-bonded clusters, respectively, such as those shown in Fig. 6 (3). They proposed that if the cluster is large, as in Fig. 6(A), the "flip-up" molecules (those with O-H bonds perpendicular to the surface) which are present in the middle of the cluster desorb preferentially. This leaves the smaller clusters shown in Fig. 6(B) (3). These smaller clusters are more stable and their dissolution results in a separate desorption state at higher temperatures, A_1 . The main difference between the large (A_2) and small (A_1) clusters is that the former contain molecules in the second layer with an OH bond perpendicular to the surface, whereas the latter do not. All of the second-layer molecules in the smaller (A_1) clusters have OH bonds pointed only toward the first layer, as shown in Fig. 6(B). In short, the conversion from large to small clusters requires not only loss

Figure 6. Structures of hydrogen-bonded water clusters adsorbed on Ru(001), originally proposed by Doering and Madey (3). The larger cluster shown in (A) breaks up and partly desorbs as the A_2 state, whereas the smaller clusters in (B) desorb as the A_1 state (3). Filled circles represent hydrogen atoms, open circles represent oxygen atoms in the second layer, and cross-hatched circles represent oxygen atoms in the first layer (closest to the metal surface). The water molecules labelled (a) and (b) correspond to those of Fig. 7.

Figure 7. A possible structural rearrangement which could occur in conversion between the A_2 and A_1 desorption states. The key is described in Fig. 6.

of water molecules, but also a rearrangement among remaining molecules. The rate of rearrangement must be sensitive to the difference in zero point energies between H_2O and D_2O .

For energetics reasons, it is not likely that the $A_2 \rightarrow A_1$ conversion proceeds via dissolution and re-formation of hydrogen-bonded clusters. Rather, we propose that the oxygen atoms of the cluster remain in place, and rearrangement proceeds via rotation of at least two molecules, as illustrated in Fig. 7. The four-molecule units shown in Figs. 7(A) and 7(B) are components of the extended two-layer clusters shown in Figs. 6(A) and 6(B), respectively. Within the four-molecule unit of Fig. 6(A), the second-layer molecule (labelled a) rotates so that one OH bond moves from a position perpendicular to the surface, to a position downward toward one of the first-layer molecules (labelled b). Also, molecule (b) must rotate so that one OH bond moves away from molecule (a). If molecule (b) is part of an extended cluster, this rotation may also necessitate rearrangement farther along in the cluster.

Vibrational data show that water has two frustrated rotations within the chemisorbed hydrogen-bonded cluster, for which the fundamental frequencies occur at ~ 500 and 800 cm^{-1} (2). During A_2 desorption, these modes stiffen and the fundamental frequencies increase to 700 and 920 cm^{-1} (2,4). All of these frequencies shift downward upon deuteration by a factor of 1.4 (2). If we assume that the rate-limiting step in $A_2 \rightarrow A_1$ conversion is rotation of a single molecule, then the difference in zero point energies for the H_2O and D_2O reactions, ΔE , lies between 0.20 and 0.33 kcal/mol. The predicted isotope effect at 150 K is then

$$R^* = \frac{\nu_{con}(H_2O)}{\nu_{con}(D_2O)} \exp\left(\frac{\Delta E}{kT}\right) = 2.7 \text{ to } 4.2.$$

[Here $\nu_{con}(H_2O)/\nu_{con}(D_2O)$ has been set equal to 1.4.] On the other hand, if the reaction is limited by the rate of concerted rotation of two molecules, the values of R^* are predicted to fall between 7.4 and 17.6. Concerted rotation of two molecules is consistent with the model described by Fig. 7. Both sets of predicted values fall partially within the range of the experimentally-derived values of R^* , 3.4 to 8.1, and we cannot distinguish which is the correct model at this point. However, we consider that this degree of consistency between theory and experiment is quite good, given the simplicity of the approach we have taken to both.

Finally, suppression of the A_1 state in desorption of D_2O cannot be related to a difference in structure of the adsorbed layer due to a difference in molecular size. Bond lengths and bond angles in D_2O and H_2O are identical to within hundredths of a percent in both the free molecule and in ice (11). The O-H and O-D bond lengths in the free molecule are 0.9572 and 0.9575 Å, respectively (11). The oxygen-oxygen separation along the c-axis of ice is 2.761 Å for D_2O and 2.760 Å for H_2O , under comparable conditions of temperature and pressure (11). For short hydrogen bonds (less than about 2.75 Å) the hydrogen bond length can be longer for the deuterated isotope by as much as 2% (12), but the water-water hydrogen bond exceeds 2.75 Å slightly and does not show a significant difference.

An important ramification of this work is that adsorption and desorption processes for D_2O are *not* necessarily the same as for H_2O . It is not valid to assume that D_2O is completely interchangeable with H_2O , for example, in studies of isotopic mixing between adsorbed species, nor in vibrational spectroscopies where isotopic frequency shifts are frequently used to identify the modes.

In summary, we find that the A_1 thermal desorption state of H_2O is strongly suppressed upon substitution of D_2O . Variation of heating rate during thermal desorption indicates that the A_1 state is formed by conversion from the A_2 state. We propose that this conversion is much slower for D_2O than for H_2O , so that direct desorption from the A_2 state is kinetically favored over conversion and the high-temperature state is suppressed for D_2O . The rate constant for conversion is 3 to 8 times smaller for D_2O than for H_2O . This is the first observation of an isotope effect in thermal desorption of water. An important conclusion is that D_2O cannot always be used interchangeably with H_2O in studies of surface chemistry.

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APPENDIX C:

KINETIC ANALYSIS OF THE A_2 THERMAL DESORPTION
STATE OF D_2O ON $Ru(001)$

I. INTRODUCTION

The purpose of this study was to extract the reaction order and the coverage-dependent activation energy for the A_2 state of D_2O on $Ru(001)$ from thermal desorption data.

Most analyses of thermal desorption data (1,2) begin with the assumption that the macroscopic rate of desorption, R_{des} , follows an Arrhenius rate law:

$$R_{des} = \nu (N_s)^x \exp\left(\frac{-E}{RT}\right) \quad (1)$$

where ν , x , and E may be functions of N_s . Here, ν is the pre-exponential factor, N_s is the surface concentration, x is the reaction order, E_a is the energy barrier to desorption, R is the gas constant and T is the surface temperature. In an experiment where pumping speed is relatively fast, we have

$$P = cR_{des} \quad (2)$$

where P is the measured quantity, i.e., the instantaneous pressure of desorbing species, and c is a proportionality constant which is determined by the experimental apparatus.

Equation (1) may not be appropriate to describe desorption kinetics if several competing microscopic processes determine the macroscopic desorption rate (e.g., 3), or if the desorption rate at given N_s and T

depends also on the initial surface coverage. The latter possibility could be realized if the total desorption rate were to depend on adlayer configuration, which in turn were determined by the kinetics of adlayer rearrangement during the thermal ramp. Here we take equation (1) as our starting point, in order to use the data analysis schemes suggested by King (4) and Falconer and Madix (5), although under some conditions it yields physically meaningless results and is clearly inappropriate.

II. EXPERIMENTAL RESULTS

Both the King and Falconer-Madix analyses begin with a family of $N_s(T)$ curves, such as those shown in Fig. 1 for the A_2 state of D_2O . Taking the logarithm of all terms in Eq. (1), and combining with Eq. (2), we obtain

$$\ln(P) = \ln(cv) + \ln(N_s) + \left(\frac{-E}{RT}\right) \quad (3)$$

Since the pressure (corresponding to the desorption rate) for each combination of N_s and T can be found from the original desorption trace, an Arrhenius plot of $\ln P$ vs. T^{-1} can be constructed corresponding to several (constant) coverages, after King (4). The range of coverages used in our isosteres falls between the two horizontal dashed lines of Fig. 1, i.e. between 5 and $19 \times 10^{13} \text{ cm}^{-2}$ ($\theta = 0.03$ to 0.12). The resultant Arrhenius plots, $\ln P$ vs. T^{-1} , are shown in Fig. 2, where the changing slopes indicate a coverage-dependent activation energy. The values obtained for $E(N_s)$ are represented by the circles in Fig. 3. Note that values of the activation energy at low coverages are negative, which is not physically reasonable.

It can be seen from Eq. 3 that the intercepts, i , of the Arrhenius plots of Fig. 2 must be given by

$$i = \ln(cv) + \ln(N_s) \quad (4)$$

Figure 1. Surface concentration, N_s , as a function of surface temperature of the A_2 desorption state of D_2O for initial coverages of 0.5, 0.3, and 0.1 monolayers of D_2O . Average heating rate over this temperature range is 10 K/s. (See text for explanation of vertical and horizontal lines.)

Figure 2. Arrhenius plots from King thermal desorption analysis

Figure 3. Desorption energies as a function of surface coverage
 Shown above are the coverage dependent activation energies to desorption as determined by both the King and Falconer-Madix methods. (See text for explanation of the two sets of Falconer-Madix data.)

From our data, i does not vary linearly with $\ln(N_s)$ as shown in Fig. 4, which in turn indicates that ν or x , or both, are coverage-dependent.

Using the Falconer-Madix approach, desorption rate isotherms ($\ln P$ vs. $\ln N_s$ at constant T) are constructed. These isotherms should be linear, with slope x , if x , ν and E are independent of coverage (cf. Eq. 3). Figure 5 shows a series of isotherms for the A_2 desorption state of D_2O . The temperatures of the isotherms fall between the two vertical dashed lines of Fig. 1. The isotherms tend to deviate slightly from linearity at low temperatures with slopes ranging from 1.4 at 197 K to 1.9 at 171 K, indicating an (effective) desorption order greater than unity. This is consistent with the downward shift in peak temperature which is observed with increasing initial coverage for the A_2 state (3). The non-linearity may reflect a coverage-dependence in x , ν , and/or E . Since the data tend to deviate strongly from linearity at low temperature, they are also fit with an n th-order polynomial for the sake of subsequent analysis.

Arrhenius plots can then be constructed from the data of Fig. 5, at constant coverage. The range of coverages to which our data can be applied directly in this analysis lies between 12 and $19 \times 10^{13} \text{ cm}^{-2}$ ($\theta = 0.08$ to 0.12). Some of the Arrhenius plots for this coverage regime are shown in Fig. 6. The values of $E(N_s)$ thus obtained are shown in Fig. 3 where squares represent values from the linear fits to the isotherms, and triangles represent values from the polynomial fits. The activation energies tend to be about 2 kcal/mol lower for the polynomial fits than for the straight line fits.

Figure 4. Plot of the intercept, i , vs. $\ln(N_s)$

Figure 5. Isotherms from Falconer-Madix thermal desorption analysis

Figure 6. Arrhenius plots from Falconer-Madix thermal desorption analysis

III. CONCLUSIONS

The results of this analysis show that both the King and Falconer-Madix methods indicate a coverage dependent activation energy. The King method indicates a coverage dependent preexponential factor as well. An increase in the activation energy with increasing coverage is indicated by the King method, whereas the Falconer-Madix shows a slight decrease. If we only consider hydrogen bonding as the major contributor to the stability of the D_2O clusters then as coverage increases an increase in the activation energy of desorption would be expected for this system as suggested by the King results. However, we know that for D_2O on Ru(001) the total desorption rate depends also on adlayer configuration, which in turn determines the kinetics of adlayer rearrangement during the thermal ramp (3). This rearrangement would be expected to be easier for smaller clusters and may result in a decrease in the activation energy to desorption with increasing coverage as suggested by the Falconer-Madix results. In any case, the activation energies for low coverages determined by both methods tend to group close to the activation energy of 10.8 kcal/mol reported by Doering and Madey for the A_2 state of H_2O on Ru(001) (6) which was calculated with Redhead's equation. The erroneous results such as that found for the activation energies as a function of coverage from the King analysis, may result because Equation (1) is not appropriate to describe desorption kinetics if several competing microscopic processes determine the macroscopic desorption rate such as that for D_2O on Ru(001) (3), or if the desorption rate at given N_s and T

depends also on the initial surface coverage. It should also be noted that the number of desorption traces utilized in this work was rather limited. This may also serve to restrict the accuracy of the kinetic parameters obtained.

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