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Electronic and CO chemisorption properties of ultrathin Pd films vapor deposited on Au(111)

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We present a study of the electronic and CO chemisorption properties of ultrathin Pd films on Au(111). Using ultraviolet photoemission spectroscopy (UPS) we examined the valence-band electronic structure of Pd films for different thicknesses. The UPS spectrum of a Pd monolayer on Au(111) shows a narrow Pd 4*d* density of states at 1.6 eV below the Fermi level and a reduced density of states near the Fermi level. The valence-band spectra of a Pd monolayer annealed to increasing temperatures was also examined. As a result of Pd-Au interdiffusion, the Pd density of states is seen to sharpen and shift closer to the Fermi level. In the valence spectra of a Pd monolayer annealed above 300 K we identified a feature near 3.5 eV which we attribute to a Pd-Au hybrid state. Using UPS, temperature programmed desorption (TPD), and high-resolution electron-energy-loss spectroscopy (HREELS), we also examined the CO chemisorption properties of ultrathin Pd films on Au(111). From CO TPD experiments we estimate that the activation energy for CO desorption from a Pd monolayer on Au(111) is 32 kcal/mol. HREELS spectra of CO adsorbed on a Pd monolayer on Au(111) show that CO occupies threefold bridge sites at low CO coverage and both the twofold bridge and atop sites at saturation CO coverage. From these results we conclude that the CO chemisorption properties of a Pd monolayer on Au(111) are very similar to those of Pd(111) surfaces, which is striking in view of the large differences between the valence-band electronic structure of these two surfaces.

I. INTRODUCTION

A great deal of recent attention has focused on the physics and chemistry of Pd thin films on several metal single-crystal surfaces, owing to the significant differences in the structural, electronic, and chemical properties between these films and bulk Pd. Pd films are of particular interest in these studies since the observed changes in the CO chemisorption properties are greater than those observed on Ni or Pt. For example, a comparison of CO desorption from Ni, Pd, and Pt monolayer films supported on W(110) to that from bulk Ni, Pd, and Pt(111) samples shows that the CO desorption temperature decreases by 50 and 60 K for the Ni (Ref. 1) and Pt (Ref. 2) monolayer films, respectively, but a surprising 180–195 K for the Pd monolayer.[3,4] The electronic structure of Pd monolayers on different substrates has also been observed to be considerably different than that of bulk Pd, showing a low density of states at the Fermi level (E_F) characteristic of the group 1*B* (Cu, Ag, and Au) metals. This alteration of the electronic structure is not strongly dependent on the choice of the substrate, with similar changes seen for Pd thin films on Ta(110),[5,6] Nb(110),[7,8] W(110),[9] Cu(111),[10] Ag(111),[11] Au(111),[12] and Al(111).[13,14] This is most striking in view of the proposed reasons why these alterations should occur, such as lowered Pd-Pd overlap (proposed for the highly strained Pd-Nb system,[15] but inapplicable to the almost unstrained Pd-Ag and Pd-Au systems), *d*-state covalent interactions between the substrate and adsorbate [also proposed for Pd-Nb (Ref. 16)], or charge transfer.[17]

Much of the previous work on CO chemisorption on Pd thin films was done with refractory, early transition metals as substrates. These metals exothermically alloy with Pd,[18] indicating interaction between the Pd *d* states and those of the substrate. Owing in part to the lower free energy of surfaces of bulk Pd than that of the single-crystal surfaces of refractory metals, Pd forms thermally stable monolayers even at high temperatures.[19–23] The refractory metal substrates have a bcc crystal structure, and the structural differences between the bcc substrate and Pd (which in the bulk has a fcc crystal structure) result in Pd monolayers exhibiting considerable lattice strain. The most common refractory metal surface plane used in these studies is (110), which resembles the closest-packed fcc(111) face except with a change in the apex angle from 120° to 108°, and induces a lattice strain on the order of 15–20 % in the pseudomorphic Pd monolayer. This lattice strain has been invoked as a possible cause of the alteration of the Pd electronic structure, since Pd-Pd overlap in the adlayer is lessened with respect to bulk Pd.[15] However, ultraviolet photoemission spectroscopy (UPS) studies of a Pd monolayer of fcc(111) structure which forms with almost no lattice strain on the Ta(110) surface shows a very similar electronic structure to that of the highly strained pseudomorphic Pd monolayer.[6] Also, CO (Refs. 24 and 25) and H_2 (Ref. 26) chemisorption properties have been shown to be essentially the same for these two different structures of the Pd monolayers on Ta(110). This rules out lattice strain as the major cause for the alterations in the chemical properties of Pd monolayers on single crystals of refractory metals, a result consistent with those on other strained metal overlayer systems.[1]

The characteristics of Au(111) are almost diametrical to those of the refractory metal substrates commonly used to support Pd films. Au and Pd form almost ideal, substitutionally random alloys at all concentrations.[27] Pd

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and Au share the fcc crystal structure, with bulk lattice constants differing by less than 5% [indeed, there is evidence that the Au(111) surface undergoes a reconstruction that relaxes the surface mesh to almost exactly coincide with that of Pd (Ref. 28)]. So lattice strain is not expected to be a large driving force for altering the properties of a Pd monolayer on Au(111). Also, the work function (ϕ) and the electronegativity (χ) of Au ($\phi=5.3$ eV, $\chi=1.4$) are closer to Pd ($\phi=5.6$ eV, $\chi=1.4$) than some of the early transition metals, e.g., Ta [$\phi=4.8$ eV for Ta(110), $\chi=1.3$]. Moreover, x-ray photoemission spectroscopy (XPS) measurements of the Pd 3*d* and Au 4*f* core levels for a Pd monolayer on Au(111) and Pd/Au alloys[29] show very small shifts (<0.2 eV for Pd relative to bulk Pd, and no shift for Au) indicating small perturbations in the charge density near Pd or Au. In contrast, Pd monolayers on refractory metals surfaces such as Ta, W, and Mo, where the chemical properties of the Pd monolayer are dramatically altered, have fairly large Pd 3*d* core-level shifts.[30] Based on these observations one expects less significant alterations in the chemisorption properties of a Pd monolayer on Au(111). Surprisingly, Shen *et al.*[31] reached different conclusions. From high-resolution electron-energy-loss spectroscopy (HREELS) and UPS studies of CO adsorption on Pd deposited on Au(111) at 300 K, they concluded that a Pd monolayer on Au(111) is inert to CO adsorption due to a reduced density of Pd *d* states near E_F, much like Pd monolayers on refractory metal substrates. We have recently reinvestigated the growth and film structure of Pd deposited on Au(111), and concluded that a Pd monolayer cannot be formed at 300 K (Ref. 29) due to alloying. It is thus appropriate to make new and additional studies of CO chemisorption on well-characterized Pd films on Au(111), especially on Pd films deposited at low temperature where it was shown that pure Pd films can be formed.[29] Our results, which will be discussed herein, clearly show that the Pd monolayer exhibits CO chemisorption properties similar to those of the (111) surface of bulk Pd, even though the photoemission valence spectra still show a reduced density of states near E_F.

II. EXPERIMENTAL METHODS

The experiments were performed in a UHV system described in detail elsewhere.[32] This system has an operational base pressure less than 1×10^{-10} torr, and is equipped with a double-pass cylindrical mirror analyzer (CMA) for Auger-electron spectroscopy (AES), a quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD), a four-grid low-energy electron-diffraction (LEED) optics, and a HREELS spectrometer for vibrational spectroscopy. The Au(111) single-crystal (Atomergic, 5N purity) was mounted on a rotatable stage with provisions for cooling to 125 K or resistive heating to 1200 K, and was cleaned by Ar^+ sputtering (5×10^{-5} torr, 800 V) and subsequent annealing to 1000 K until no contaminants were detected by AES.

Palladium deposition was carried out by resistively heating a 0.25-mm-diameter tungsten wire that had a 0.1-mm Pd (Alfa, 99.997%) wire wrapped around it. The Pd films on the Au(111) surface were removed by sputtering the crystal with Ar^+ (5×10^{-5} torr, 800 V) at 125 K for typically 10 min, followed by annealing to 1000 K in UHV for 10 min. The complete loss of the intense Pd (330 eV) Auger transition assured complete removal of Pd from the surface region. Pd films were deposited at 125 or 300 K. During Pd evaporation the UHV pressure remained below 2×10^{-10} torr.

CO doses were all made using a microcapillary array doser. CO exposures carried out to achieve saturation coverage required less than 1 L ($L=10^{-6}$ torr s) for all the Pd films studied.

CO TPD measurements used a 7 K/s temperature ramp. The UPS experiments were performed using a differentially pumped He resonance lamp, and the spectra were recorded by using a CMA with a resolution of 0.40 eV for He II spectra and 0.24 eV for He I spectra. HREELS spectra were taken with a primary beam energy of 5.8 eV and an energy resolution of 90 cm^{-1}. Count rates at the elastic peak were on the order of $1-10\times10^3$ counts/s.

III. RESULTS

For all of the experiments discussed herein, the intensities of the Pd (330 eV) and Au (69 eV) Auger transitions were monitored as a function of Pd deposition time, and the Auger uptake curves derived from these intensities were used to determine the appropriate Pd film thickness. We have recently reported our studies of Pd deposition on Au(111) in which the growth properties and surface concentrations of Pd films on Au(111) were addressed in detail.[29] Pd adlayers with nearly uniform thickness of one, two, or three monolayers can be prepared by deposition of Pd on Au(111) at 125 K. Overlayer coverages θ_{Pd} are defined relative to the Au(111) surface-atom density which is equal to 1.39×10^{15} atoms/cm^2. Annealing the clean films at temperatures exceeding 220 K causes alloying to occur and results in significant surface concentrations of Au.

A. UV photoemission

1. Pd overlayers on Au(111)

He I (21.2 eV) and He II (40.8 eV) UV photons were used to investigate the electronic properties of the Pd/Au(111) surface. Photoelectrons emitted from the valence bands of Pd and Au have kinetic energies of 10–15 eV for He I excitation and 30–35 eV for He II light. These kinetic energies correspond to electron mean free paths of 4–2 Pd monolayers and one Pd monolayer, respectively.[33] The shorter mean free path for photoelectrons excited by He II light makes the He II spectra much more surface sensitive.

Figure 1 displays several angle-integrated He I spectra taken from Pd films of various thicknesses deposited on Au(111) at 125 K. The spectrum from clean Au(111) exhibits peaks at −2.7, −4.3, −5.0, −6.3, and −7.3 eV. These peaks stem from the 5*d* bands of Au. The flat region in the spectrum between −1.7 eV and the Fermi lev-

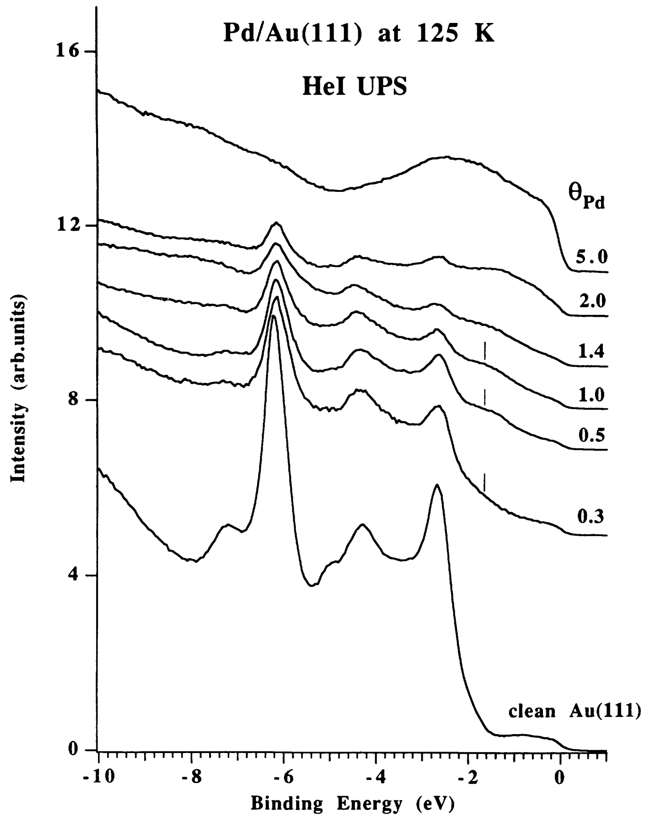

FIG. 1. He I UPS spectra obtained from Pd films of various coverages that have been vapor deposited on Au(111) at 125 K.

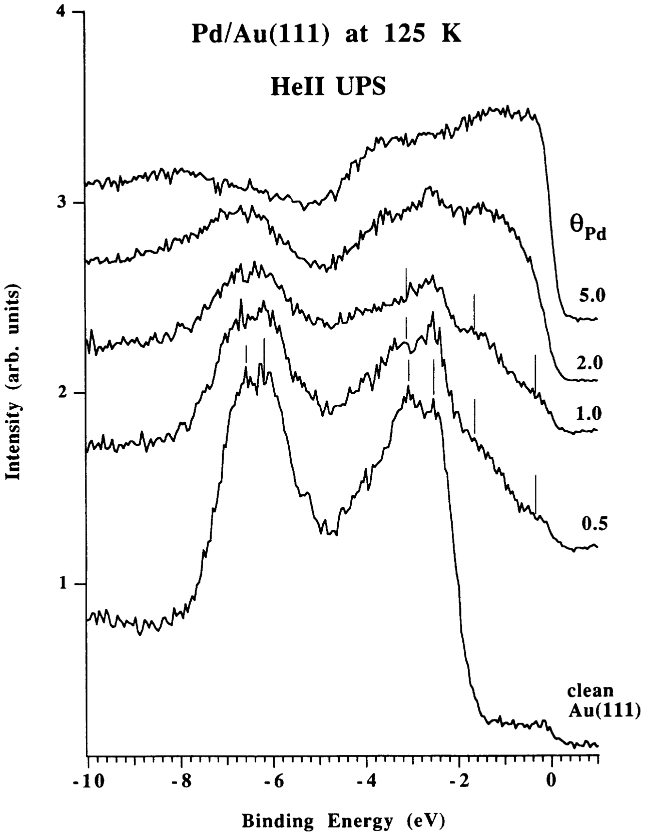

FIG. 2. He II UPS spectra obtained from Pd films of various coverages that have been vapor deposited on Au(111) at 125 K.

el corresponds to photoelectron emission from the Au *s*-*p* band (also referred to as the *s*-*p* plateau). Figure 2 shows angle-integrated He II spectra taken from several similar Pd films on Au(111). The clean Au(111) He II spectrum exhibits less structure and different peaks than the He I photoemission spectrum due to cross-section changes. With He II, peaks stemming from the Au 5*d* bands were seen at −2.7, −3.1, −6.3, and −6.6 eV. The *s*-*p* plateau was also visible near the Fermi level. The He I and He II spectra for clean Au(111) are consistent with electron energy distribution curves (EDC's) derived from a band-structure calculation by Christensen and Seraphin,[34] and with angle-resolved photoemission measurements by Mills *et al.*[35]

In the He I spectra, the addition of Pd to the Au(111) surface up to a monolayer induces a single photoemission peak at −1.6 eV which is derived from the Pd 4*d* valence band. Deposition of Pd films thicker than one monolayer increases photoelectron emission near the Fermi edge and also gives rise to very broad features at higher binding energies extending up to −5.0 eV. This is clearly seen in the He I spectrum following deposition of two monolayers of Pd. We note that after deposition of only 0.3 monolayer of Pd, the photoemission peaks associated with the Au 5*d* valence electrons are attenuated more strongly than is expected from the electron mean free paths of 2–4 monolayers. It is possible that this attenuation arises from angle-dependent blocking effects or diffraction by the Pd adatoms of photoelectrons emitted from the Au atoms.

In the He II spectra, deposition of Pd up to one monolayer induces a Pd peak at −1.6 eV, a shoulder at −0.4 eV, and an attenuation of the Au-derived peak at −3.1 eV. Deposition of Pd films thicker than a monolayer increase photoelectron emission near the Fermi level and induce broad features extending from 0 to −5 eV. In order to better show the contribution of the Pd 4*d* band to the photoemission spectra, the He II spectrum from clean Au(111) was subtracted from the He II spectrum of the Pd monolayer. The resulting difference spectrum[36] is shown in Fig. 3. This spectrum clearly shows that the contribution from the Pd monolayer to the surface electronic density of states is limited to a relatively narrow peak centered at −1.6-eV binding energy, and that the electron density near the Fermi level is drastically reduced compared to that for thick Pd films.

Figure 4 illustrates the variation of the work function of these surfaces as a function of Pd coverage. The value of the work function is obtained as the difference between the photon energy and the energy interval separating the low-energy photoemission cutoff and the Fermi level. The clean Au(111) surface yields a work function of 5.43 eV, which is slightly greater than the work-function value of 5.3 eV reported by Potter and Blakeley.[37] The work function decreases sharply by approximately 0.3 eV following Pd deposition of only 0.3 monolayer, and then remains constant around 5.25 eV for Pd coverages up to one monolayer. The work function decreases again to

5.06 eV at $\theta_{Pd}=1.4$, and then it increases to 5.2 eV at two monolayers of Pd. Finally the work function reaches a maximum value of 5.5 eV at five monolayers of Pd, which is close to the work-function value of 5.6 eV measured on clean Pd(111).[38]

The rapid drop of the work function after deposition of only 0.3 monolayer of Pd is attributed to the so-called Smoluchowski effect[39] commonly seen on rough surfaces. At this coverage, Pd atoms are relatively dispersed on the Au(111) surface with little Pd-Pd interaction allowing for a decompression of the electron charge density away from the isolated Pd atoms. The work function stabilizes over the range $0.5<\theta_{Pd}<1$, which we attributed to the formation of two-dimensional (2D) islands of Pd. The drop in work function between 1.0 and 1.4 monolayers of Pd is again associated with roughness or a small amount of highly dispersed second-layer Pd atoms on top of the first Pd layer.

2. Annealed Pd monolayer on Au(111): Pd/Au alloy

Figure 5 displays a series of He II spectra obtained from a monolayer of Pd after annealing to increasing temperatures. The Pd layer was initially deposited at 125 K. One can follow the changes in the Pd and Au electronic structures as various alloy compositions are achieved near the surface. We chose to concentrate on the He II spectra because of the relatively small escape depth of He II photoelectrons electrons emitted from the valence bands of Pd and Au.

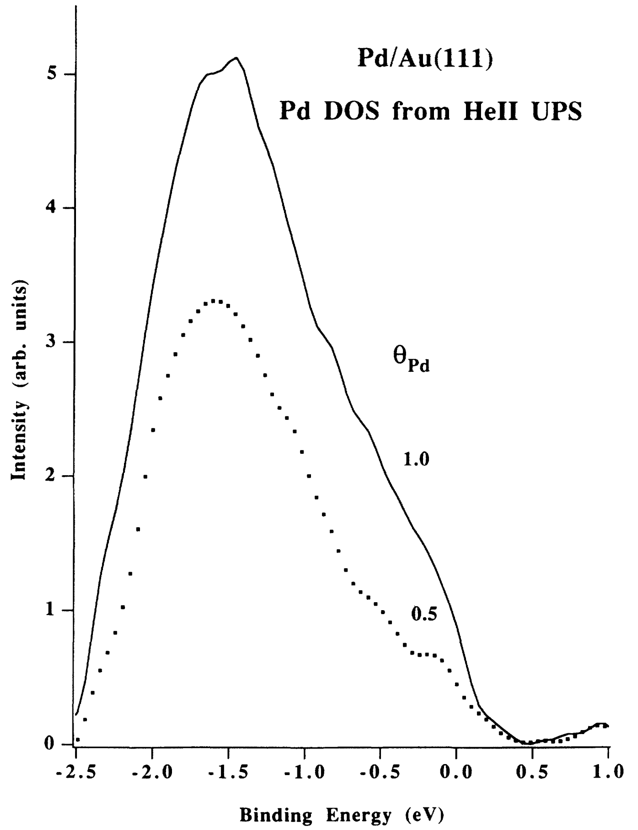

FIG. 3. The Pd DOS near E_F derived from the He II UPS spectra for a $\theta_{Pd}=1$ Pd film (full curve) and a $\theta_{Pd}=0.5$ Pd film (dotted curve).

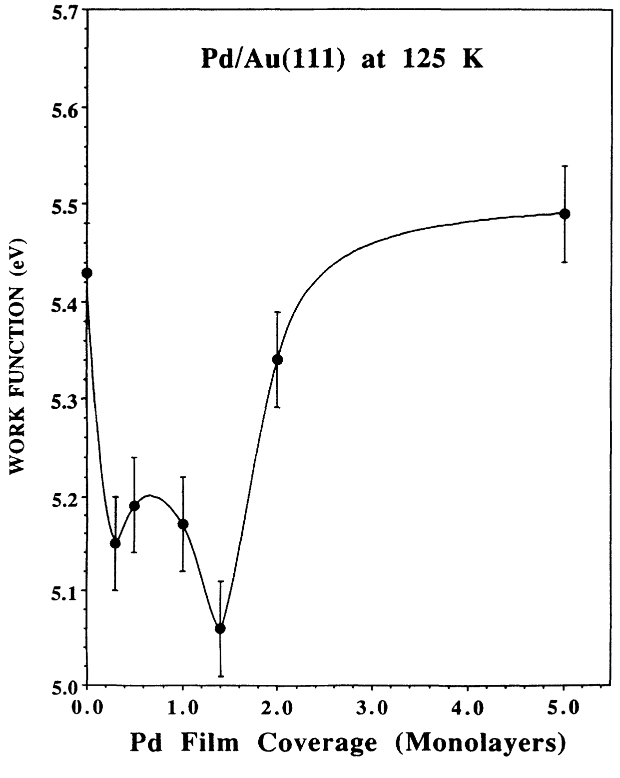

FIG. 4. The work function of Pd films vapor deposited on Au(111) at 125 K.

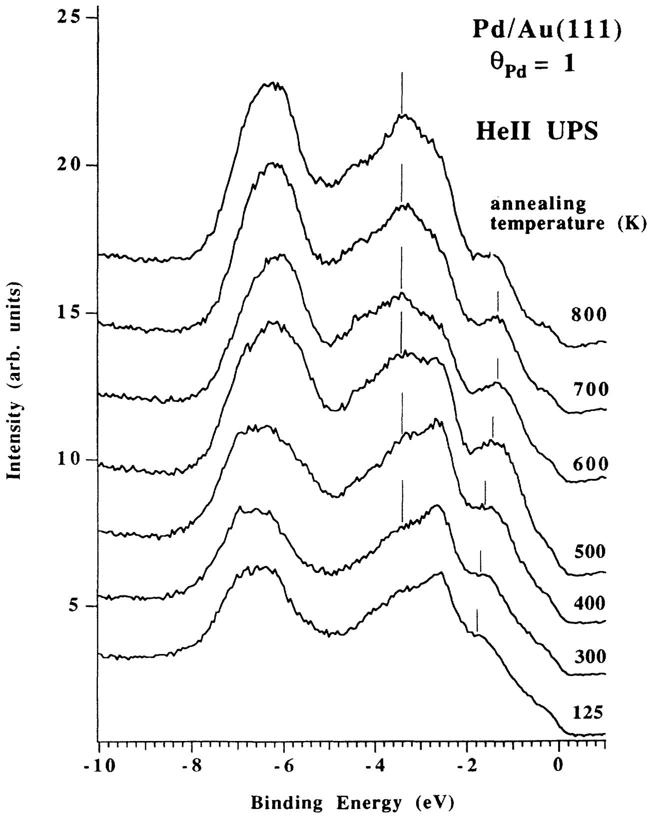

FIG. 5. He II UPS spectra obtained after annealing a monolayer Pd film deposited on Au(111) at 125 K.

In Fig. 5 the Pd 4*d* resonance at -1.6 eV sharpens and slightly shifts to -1.5 eV after annealing to 300 K. At 400 K a new peak develops at -3.5 eV, and its intensity increases as the sample is annealed to higher temperatures, while the Pd 4*d* resonance continues to sharpen and shift slowly to lower binding energy. At 600 K this latter peak has shifted to a maximum value of -1.4 eV and is clearly separated from the Au peak at -2.5 eV.

3. CO chemisorbed on Pd/Au(111)

In Fig. 6 we show the He II photoemission spectrum obtained from a monolayer of Pd exposed to 1-L CO to give a saturation coverage of chemisorbed CO. Pd deposition and the subsequent CO exposure were carried out at a substrate temperature of 125 K. The spectra in Figs. 6(b) and 6(c) show the usual double-peak structure at -11.4 and -8.4 eV associated with emission from the 4σ and $5\sigma+1\pi$ orbitals, respectively, of molecularly adsorbed CO. The spectra also show a strong reduction in the intensity of the Pd-induced peak at -1.6 eV, and the Au-derived peak at -3.1 eV. It is well known that the CO chemisorption bond to most metal surfaces involves a synergistic charge donation from the 5σ orbital to the metal *d* band and back donation from the metal *d* band to the $2\pi^*$ orbital of CO. With a larger charge transfer to the $2\pi^*$ orbital through backbonding, this corresponds to a net charge transferred from the metal to CO. The strong attenuation of the -1.6-eV peak is consistent with such a process after assignment of this peak to the Pd monolayer 4*d* band.

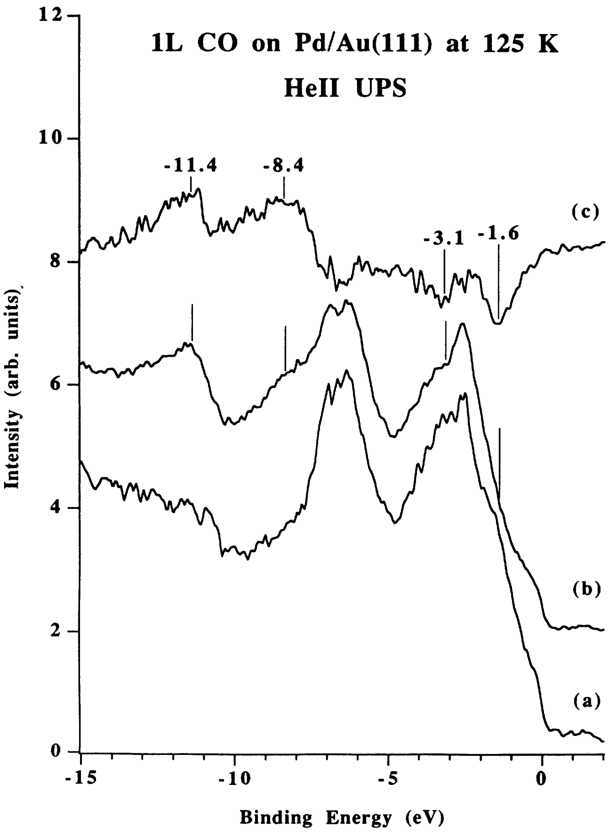

FIG. 6. (a) He II UPS spectra obtained from a monolayer Pd film deposited on Au(111) at 125 K. (b) The same Pd film after a saturation exposure of 1-L CO at 125 K. (c) Difference spectrum (b)−(a) with no scaling.

B. Temperature programmed desorption (TPD) of CO on Pd/Au(111)

It is critically important to ascertain the adsorption energy of CO on these Pd films. TPD is often a convenient method for making this determination. The interpretation of CO TPD results from Pd thin films on Au(111) are complicated by the continuous changes in the surface composition due to alloying that are likely to take place during TPD experiments. CO desorption continues until well above the onset of Pd diffusion in the absence of CO, and therefore TPD measurements may not give a reliable estimate of the different types of CO present on the Pd films and may only give a lower bound on the CO desorption activation energy (since CO desorption may be induced by Pd interdiffusion and loss of adsorption sites).

Figure 7 shows the results of CO TPD experiments conducted on several Pd films deposited at 125 K. The Pd films were exposed to 1-L CO, which gave a saturation coverage of CO. The CO TPD spectrum from a $\theta_{\text{Pd}}=0.5$ film shows three broad desorption features at 240, 350, and 440 K. This TPD spectrum exhibits much less CO desorption above 400 K than what it is usually observed from the (111) surface of bulk Pd (the CO TPD spectrum from Pd(111) near saturation CO coverage[40,41] has a peak at 480 K and closely resembles the spectrum

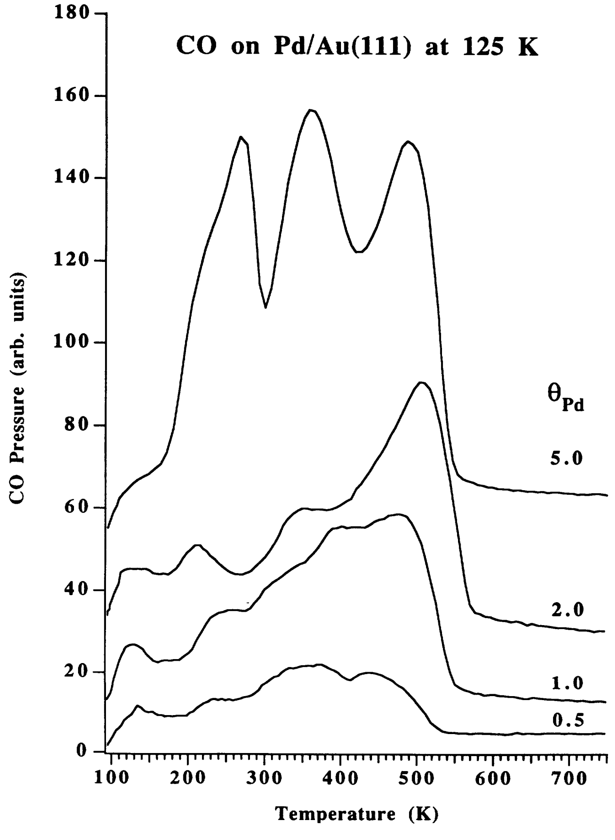

FIG. 7. CO TPD spectra obtained from Pd films of various coverages, deposited and exposed to 1-L CO at 125 K.

in Fig. 7 for $\theta_{\mathrm{Pd}}=2.0$). We believe that this result for $\theta_{\mathrm{Pd}}=0.5$ is principally due to the lack of two-dimensional islands, which was inferred from the work-function measurements discussed earlier in this section. Pd atoms are relatively dispersed on Au(111) at 125 K, preventing the formation of threefold, and to a lesser degree, twofold sites on which CO is known to be highly stable on the (111) surface of bulk Pd. This assumes, of course, little perturbation in the chemical nature of Pd due its interaction with the Au atoms. Furthermore, changes in the surface composition due to alloying, which was shown to begin at 240 K (Ref. 29) in vacuum (but may begin at a higher temperature in the presence of CO) may also cause CO to desorb at temperatures lower than expected as a result of Au interdiffusion with the Pd film.

A CO TPD spectrum from a $\theta_{\mathrm{Pd}}=1.0$ film on Au(111) is also shown in Fig. 7. In this case the spectrum shows broad features at 260, 310, 400, and 480 K. There is a large increase in CO desorption near 480 K which indicates that this Pd overlayer has extensive two-dimensional order, and with it the highly stable twofold and threefold CO adsorption sites. Using Redhead analysis[42] the activation energy of CO desorption was estimated from the desorption peak at 480 K to be ≈ 32 kcal/mol (a preexponential factor of 10^{14} s^{-1} and first-order kinetics were assumed), which is in the range of 32–35 kcal/mol (Refs. 40, 41, and 43) determined for the activation energy of CO desorption from Pd(111). Thus *the adsorption energy of CO on the Pd monolayer is similar to that on the (111) surface of bulk Pd.*

The CO TPD spectrum from a $\theta_{\mathrm{Pd}}=2.0$ film shows a development of more distinct CO TPD peaks and a further increase in the desorption of CO near 480 K (compared to that from $\theta_{\mathrm{Pd}}=1.0$). Peaks at 220, 360, and 510 K are now clearly resolved in the spectrum. In comparison to the CO TPD peaks observed on a Pd monolayer, these peaks are relatively sharper. Alloying, which reduces the Pd concentration at the surface, is more extensive for the Pd monolayer in the temperature range of CO desorption,[29] and this can explain the broader desorption peaks of CO from the Pd monolayer. Finally, Fig. 7 shows a CO TPD spectrum obtained from a $\theta_{\mathrm{Pd}}=5.0$ layer where much sharper features at 250, 380, and 490 K can be seen. In this case the CO desorption peaks at low temperatures ($T<400$ K) are much more pronounced than those seen on the (111) surface of bulk Pd. This could be due to surface roughness on this Pd layer or to changes in the Pd film composition.

In order to understand the effects of alloying and to connect our measurements to the experiments conducted by Shen *et al.*,[31] we also conducted CO TPD experiments on selected Pd films which were deposited at 300 K. The results of these experiments are shown in Fig. 8. We still see an appreciable amount of CO desorption from the monolayer, indicating that the effect of alloying at 300 K on the CO uptake on the Pd monolayer is not as drastic as concluded in the work of Shen *et al.*[31] The trend from our CO TPD spectra is the same as was seen on the Pd films deposited at 125 K, namely an increase of high-temperature CO desorption with increasing Pd coverage.

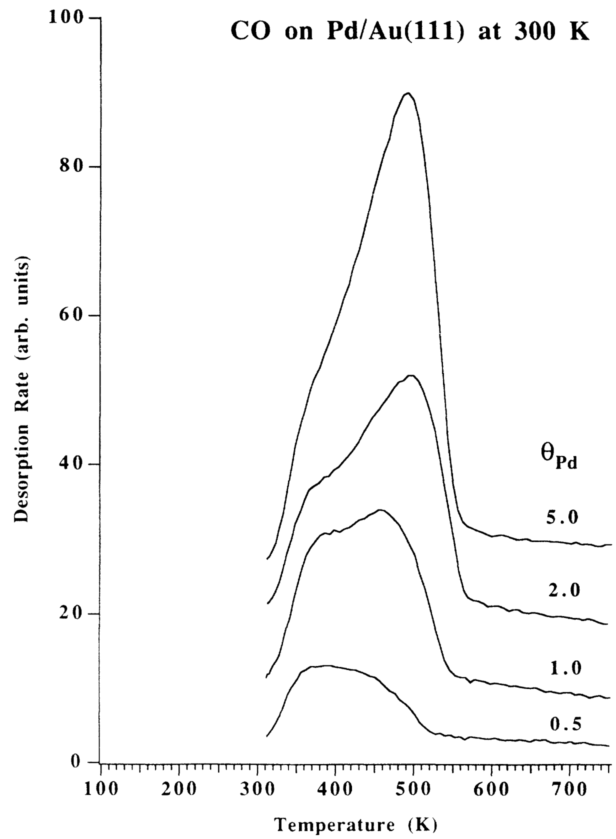

FIG. 8. CO TPD spectra obtained from Pd films of various coverages, deposited and exposed to 1-L CO at 300 K.

C. HREELS of CO chemisorbed on Pd/Au(111)

The vibrations of CO adsorbed on Pd(111) have been investigated using infrared reflection absorption spectroscopy (IRAS). Different vibrational frequencies for the C-O stretching mode were found as a function of CO coverage.[44] At $\theta_{\mathrm{CO}}=\frac{1}{3}$, a band appears at 1849 cm^{-1} and then shifts to 1918 cm^{-1} at $\theta_{\mathrm{CO}}=\frac{1}{2}$. At $\theta_{\mathrm{CO}}=0.60$ this band shifts further to 1951 cm^{-1}, and at higher CO coverages a second band appears at 2097 cm^{-1}. By comparison to C-O stretching frequencies in metal carbonyl clusters, the band at 1849 cm^{-1} was assigned to CO adsorbed in the threefold hollow sites of the Pd(111) surface. The bands in the 1918–1951-cm^{-1} range were attributed to CO adsorbed in twofold bridge sites, and the band at 2097 cm^{-1} was attributed to CO adsorbed in atop sites.

In what follows we describe HREELS results for CO adsorbed on a monolayer Pd film on Au(111), and the CO-induced vibrational losses are assigned based on the above-mentioned IRAS studies.

Figure 9 illustrates HREELS spectra from a monolayer of Pd deposited at 125 K, following 0.1- and 1.0-L CO exposures. The spectrum at 0.1-L CO corresponds to a small coverage of CO on this Pd film. The loss peak at 1850 cm^{-1} is associated with the C-O stretch frequency of CO bonded in threefold sites. The threefold site is therefore the most stable site for CO adsorbed on the Pd monolayer. The HREELS spectrum from a Pd monolayer following a saturation dose of 1-L CO shows a

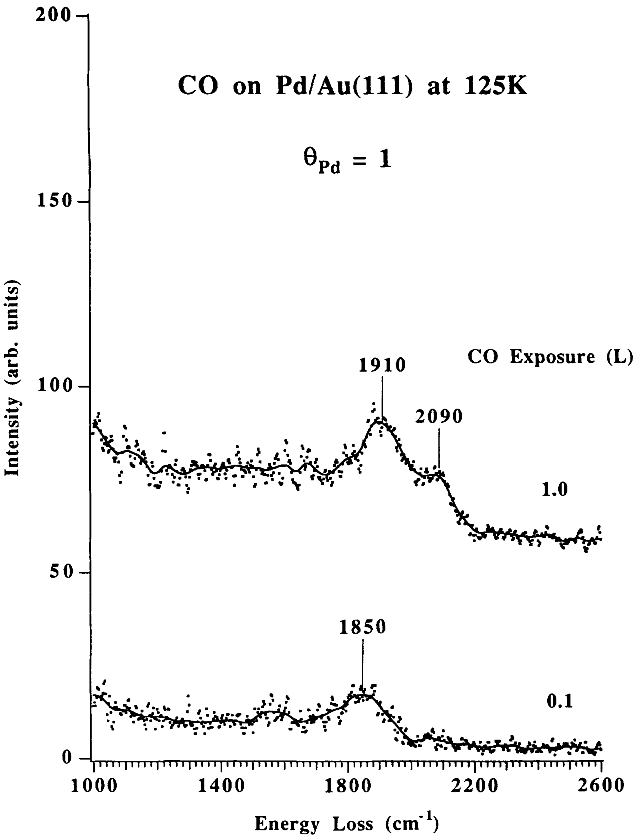

FIG. 9. HREELS spectra of two CO coverages on a monolayer Pd film deposited on Au(111) at 125 K.

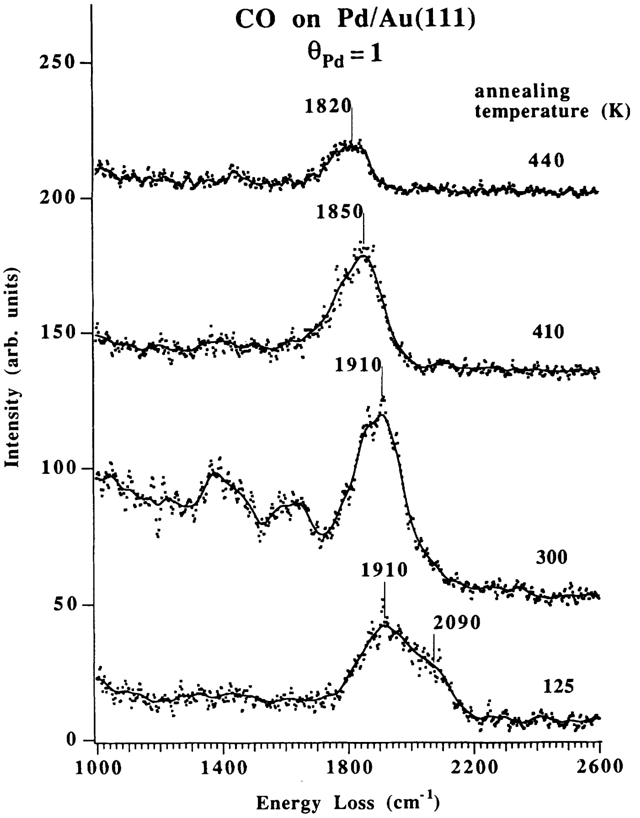

FIG. 10. HREELS spectra from a monolayer Pd film on Au(111) after exposure to 1-L CO to give a saturation CO coverage and annealing to increasing temperatures.

strong loss at 1910 cm^{-1}, and a weaker loss at 2090 cm^{-1}. These losses correspond to CO adsorbed in twofold bridge and atop sites, respectively. These results again point to the similarity of the Pd monolayer CO chemisorption properties to those of the Pd(111) surface.

In order to probe the changes in the CO adlayer that occur during TPD for a monolayer Pd film on Au(111), HREELS spectra were recorded as a function of annealing temperature. The sample was annealed for about 1 min at each temperature and then was allowed to cool down to 125 K before a HREELS spectrum was recorded. The results are summarized in Fig. 10. Annealing the sample to 300 K caused the disappearance of the 2090-cm^{-1} loss peak associated with CO in atop sites. At this temperature, the spectrum shows a prominent loss peak at 1910 cm^{-1} which is associated with CO adsorption in twofold bridge sites. This peak appears to have some contribution from a shoulder near 1820 cm^{-1}, corresponding to CO adsorbed in threefold bridge sites. Decreasing CO concentration on the surface with increasing annealing temperature increases the relative intensity of this feature as CO adsorbed in twofold bridge sites is removed and the loss peak shifts to 1850 cm^{-1} after annealing to 410 K. At 440 K this peak shifts further to 1820 cm^{-1} and its intensity is significantly reduced. Finally the 1820-cm^{-1} loss peak disappears after annealing to 500 K.

In Fig. 11 we display HREELS spectra obtained from θ_{Pd}=5.0 and 1.0 films deposited at 300 K which were subsequently exposed to a 1-L CO saturation dose. The saturation coverage of CO on the thick Pd film (θ_{Pd}=5.0) yields a narrow loss peak at 1890 cm^{-1} which is attributed to CO adsorbed in twofold bridge sites. In contrast, spectra for CO saturation coverage on a monolayer of Pd shows a much broader loss feature, attributed to two peaks at 1820 and 1870 cm^{-1}. These loss peaks are attributed to the C-O stretching frequencies of CO adsorbed in threefold and twofold bridge sites, respectively. The intensity of the loss peak at 1820 cm^{-1} is comparable to that of the 1870-cm^{-1} loss peak, which indicates that an appreciable amount of CO is adsorbed in threefold sites on the Pd monolayer at CO saturation coverage. This is in contrast to the thick Pd film where CO populates the twofold bridge sites more exclusively.

IV. DISCUSSION

The valence-band spectrum of a Pd monolayer on Au(111) is clearly much different from that of a thick Pd film surface. The Pd 4*d* band has a maximum located at −1.6 eV below the Fermi level and has a relatively narrow profile. In addition, the Pd density of states (DOS) near the Fermi level is strongly reduced. The reduced number of Pd nearest neighbors from nine at the (111) surface of bulk Pd to six in the monolayer can explain the narrow band structure of the Pd monolayer, as demon-

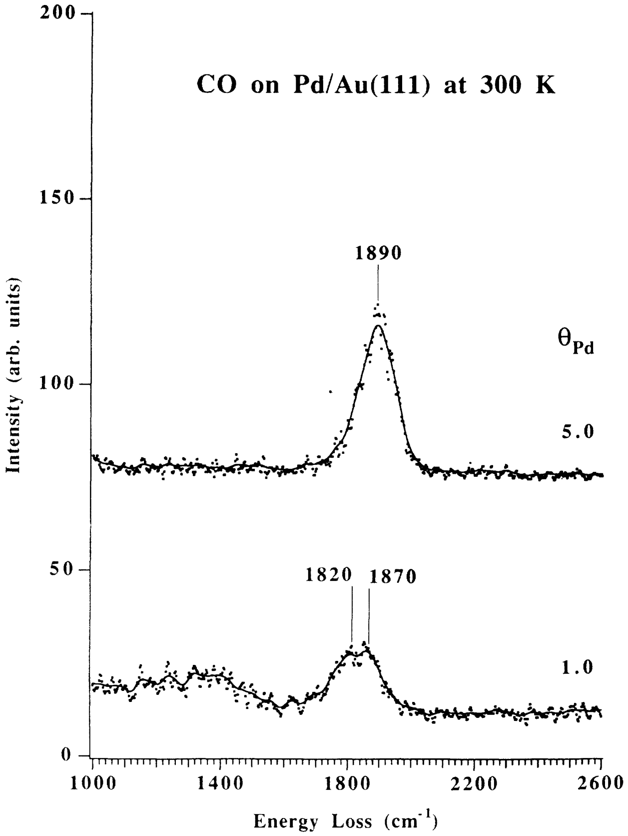

FIG. 11. HREELS spectra of CO on $\theta_{Pd}=1$ and 5 films deposited on Au(111) at 300 K after exposure to 1-L CO to give a saturation coverage of CO.

strated by local density of states (LDOS) calculations for unsupported Pd(111) performed by Kumar and Bennemann[45] using a self-consistent tight-binding scheme. The LDOS is shown to broaden extensively as the Pd layer thickness is increased from one to two layers, which was attributed to increased Pd-Pd 4*d* overlap as a consequence of an increased coordination number for the Pd atoms.

For an unsupported Pd monolayer, the calculations of Kumar and Bennemann yield a relatively broad 4*d* band ($\approx$4 eV), which is dominated by two peaks separated by $\approx$1.4 eV. In contrast, the valence-band spectra of a Pd monolayer on Au(111) show a relatively narrow Pd 4*d* band. The Pd monolayer 4*d* band width is determined from the full width at half maximum (FWHM) to be $\approx$1.2 eV (see Fig. 3). This comparison simply indicates that Pd-Au(111) interactions should not be neglected in order to understand these differences, as one might incorrectly assume from the relatively inert chemical properties of Au surfaces.

There is clear evidence from the valence band spectrum in Fig. 2 for a monolayer of Pd on Au(111) that the Au valence band is altered significantly near -3.1 eV. The attenuation of the photoemission peak at -3.1 eV (and to a lesser degree at -6.6 eV) suggests that some Pd 4*d*–Au 5*d* interaction which removes some *d* character from the Au 5*d* states induces a hybrid state. While the spectra in Fig. 2 do not clearly show the presence of such a state for the monolayer, the spectra in Fig. 5 show the appearance of photoemission peak at -3.5 eV after annealing the Pd monolayer above 400 K which could be attributed to a Pd-Au hybrid state associated with Pd-Au alloying. The Pd-Au interaction in the alloyed structure and Pd monolayer must be similar, except that in the latter configuration this interaction is reduced (due to the reduced number of Au-Pd nearest neighbors) and therefore the hybrid state contribution in the photoemission spectra is diminished.

The electronic structure of Au alloys has been the subject of several investigations. The most surprising results have been the Au Mössbauer isomer shift (attributed to increased negative charge density at Au) and the increased Au 4*f* binding energy (associated with reduced charge density at Au).[46–50] These apparently conflicting results have led to a charge-compensation model:[46] Au loses 5*d* electron density through hybridization upon alloying, but this loss is largely compensated for by a gain of conduction electrons (*s*-*p* electrons) so that charge neutrality is maintained. The validity of this model has been recently confirmed by Sham and co-workers[51,52] in an experiment where the unoccupied Au 5*d* levels were detected using x-ray absorption near-edge structure (XANES) measurements.

The photoemission spectrum of a Pd monolayer on Au(111) shows an increased electron density near the Fermi level (at ~ -0.4-eV) relative to the clean Au(111) surface. This could be due to the Pd 4*d* band, but alternatively it could be due to increased Au *sp* electron density which would compensate for the attenuation in the Au 5*d* density of states at -3.1 eV. Support for this alternative assignment comes from examining the photoemission spectra of the CO-covered Pd monolayer shown in Fig. 6. The adsorption of CO induces a strong attenuation of the Pd 4*d* peak at -1.6 eV, but the shoulder at -0.4-eV remains strong. This indicates that the -0.4-eV feature is probably not due to a Pd 4*d* resonance since it is not attenuated as a consequence of the Pd-CO interaction (which involves the strong 4*d*-2π^* backbonding), but is rather due to an increased population of the Au *sp* band.

It appears from XANES measurements that the compensation mechanism also applies to Pd alloys and intermetallic compounds.[53] The possibility that Pd *sp*, or simply *s*, orbitals might be occupied, and the Pd 4*d* band character reduced should not be overlooked. Thus, the -0.4-eV feature can also be explained by the increased density of *s* electrons at the Pd atoms.

In conclusion, we can state that the Pd-Au interaction involves Au 5*d*–Pd 4*d* bonding which generates a state that lies deep below the Fermi level (-3.5 eV). This state is located within the Au 5*d* band, and this suggests that the state retains a strong Au 5*d* character. This, on the other hand, implies that the Pd 4*d* band loses some of its *d* character, and that the charge density involved in the Pd-Au bond is concentrated mostly at the Au atom. Within this picture, *d*-to-*s* charge compensation is probably negligible for Au, but not for Pd. As mentioned previously, the Pd monolayer valence band is narrower than predicted by the calculations of Kumar and Bennemann on an isolated Pd layer, and this cannot be solely associated with the reduced coordination number of Pd. The narrowing of the Pd valence band for the monolayer is probably associated with the presence of Pd *s* electrons which increase the screening of the Pd 4*d* electrons and thus reduce the overlap of the Pd 4*d* orbitals.

Sharpening of the Pd 4*d* band near the Fermi level was observed upon deposition of Au on Pd(111) in a UPS study by Weissman-Wenocur *et al.*[26] This sharpening was considered as an unusual phenomenon by these authors. The type of Pd-Au interaction discussed above might account for this observation. Weissman-Wenocur *et al.* also examined the changes in the electronic structure of the Au/Pd system upon alloying. Their data show a feature near -4.0 eV which they attribute to a Pd-Au hybrid state.

We find that the Pd 4*d* band sharpens and shifts closer to E_F upon alloying of Pd with Au (see Fig. 5). In this case the narrowing of the band is attributed largely to reduced Pd 4*d* orbital overlap, and the shift to lower binding energy is associated with increased screening (mostly by Au *sp* electrons) of the Pd 4*d* holes formed by the photoemission process.

The structure of the CO TPD spectra changes significantly when the Pd film thickness is varied. Most of the CO adsorbed on a monolayer of Pd on Au(111) was seen to desorb at temperatures higher than 400 K. The desorption energy of CO from this monolayer was estimated to be 32 kcal/mol, which is comparable to the desorption energy of CO from Pd(111) of 32–35 kcal/mol.[40,41,43] However, by measuring the areas under the CO TPD curves, the saturation coverage of CO on the Pd monolayer at 125 K is 45% smaller than that of CO on a thick Pd film. This indicates that the Pd monolayer does not possess the full chemical properties of the Pd(111) surface. The adsorption of CO on a particular Pd site induces local changes in the electronic structure of the Pd monolayer which can extend to neighboring sites and therefore affect their chemical properties. Strong adsorption of CO molecules on metals reduces the electronic charge at surface metal atoms through metal (d)-CO($2\pi^*$) backbonding. On the Pd(111) surface these alterations are probably not severe because of the ability of the Pd substrate to compensate for this effect. On the other hand, for the Pd monolayer on Au(111) this charge compensation is probably limited because of the weaker Pd-Au interaction. Evidence for this compensation can be inferred from the photoemission spectra in Fig. 6. The adsorption of CO on a Pd monolayer also produces an attenuation in the Au electronic density of states near -3.1 eV. However, this compensation, which stabilizes the Pd monolayer, is not enough to restore the local electronic properties in the Pd monolayer near the CO adsorption sites.

The vibrational spectra of CO adsorbed on a Pd monolayer on Au(111) deposited at 125 K and the Pd(111) surface are very similar. At low CO coverage, the threefold sites are the most stable, and CO populates mostly the twofold bridge sites at higher coverages. A small amount of CO is also adsorbed in atop sites at these high CO coverages.

The saturation coverage of CO on a monolayer of Pd deposited at 300 K is 60% less than that of CO on a thick layer deposited at 300 K. At this temperature the reduction in the saturation coverage of CO is more dramatic than that of CO on a monolayer Pd film deposited at 125 K. This is due to a reduction in the Pd concentration from alloying that was shown to take place at 300 K.[31]

For a saturation coverage of CO on a Pd monolayer deposited at 300 K, the HREELS spectrum shows that CO populates both the threefold and twofold bridge sites in contrast to the thick Pd film [which exhibits the physical and chemical properties of the Pd(111) surface] where CO populates the twofold bridge sites exclusively. These results can be related to the availability of "pure" twofold bridge sites on the Pd monolayer, i.e., sites with no adjacent Au atoms which are present at the surface of a Pd monolayer after alloying at 300 K. Local electronic alterations can explain the reduced stability of twofold bridge sites after an adjacent Pd atom is substituted by an Au atom.

Based on the CO TPD experiments and the HREELS results we can state that the chemisorption properties of the Pd monolayer on Au(111) are fairly close to those of the (111) surface of bulk Pd. This is in stark contrast to the situation for Pd monolayers on refractory metal surfaces such as Ta(110) (Refs. 24 and 25) and Mo(100),[54] where the CO chemisorption properties are greatly altered (strongly reduced CO desorption energies and destabilization of the CO bridge-bonding sites). However, we have seen that the Pd monolayer on Au(111) shows a reduced density of states near the Fermi level which is similar to the Pd monolayers on the refractory metal surfaces. For a Pd monolayer on Au(111), the Pd *d* band is much closer to the Fermi level (-1.6 eV) than for Pd monolayers on refractory metal surfaces (about -2.5 eV or lower). Since CO chemisorption on metals is known to require a strong metal(d)-CO($2\pi^*$) interaction, the strength of the CO chemisorption bond is strongly related to the position of the Pd *d* states relative to the Fermi level. Evidently, the dependence of the CO bond strength on the Pd *d* band-binding energy is not initially very strong [since a Pd monolayer on Au(111) and the Pd(111) surface have very similar chemistry], but clearly a strong effect is triggered if the Pd *d* band falls below 1.6 eV to 2.5 eV below E_F. Thus we believe that the fundamental differences between the Pd monolayer on Au(111) and on the surfaces of refractory metals lies in the position of the Pd *d* band below E_F. The Pd-substrate interaction is governed by the overlap of the Pd 4*d* and substrate metal *d* states which affects the Pd *d* band-binding energy relative to the Fermi level. Strong bonding interactions of Pd with the early transition-metal substrates, similar to those that occur in the intermetallic compounds formed by these metals with Pd, cause larger shifts in the Pd *d* bands than occur on the Au(111) surface. An additional variable may also be active in controlling CO bonding on the Pd monolayers. The filling of the Pd *s* band is highly dependent on the position of the Fermi level with respect to the vacuum level, and so for metal surfaces of low work function such as the (110) surfaces of refractory metals the overlap of the Pd *s* states with the *d* states of the substrate metal below the Fermi level may result in an altered electronic configuration for Pd. It is possible that the highly repulsive nature of the Pd *s* orbital and the change in the occupancy of this band for the Pd monolayer on different substrates plays an important role in destabilizing CO on the Pd monolayer. For example, recent calculations by Smith and Carter[55] show that CO binds weakly with Pd if the metal valence *s* orbital is occupied.

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[1] P. J. Berlowitz, C. H. F. Peden, and D. W. Goodman, in *Physical and Chemical Properties of Thin Metal Overlayers and Alloy Surfaces,* edited by O. M. Zehner and D. W. Goodman, MRS Symposia Proceedings No. 83 (Materials Research Society, Pittsburgh, 1987), p. 161.

[2] R. A. Demmin, S. M. Shivaprasad, and T. E. Madey, Langmuir **4**, 1104 (1988).

[3] P. J. Berlowitz and D. W. Goodman, Langmuir **4**, 1091 (1988).

[4] Y. B. Zhao and R. Gomer, Surf. Sci. **239**, 189 (1990).

[5] M. W. Ruckman, P. D. Johnson, and M. Strongin, Phys. Rev. B **31**, 3405 (1985).

[6] M. W. Ruckman, V. Murgai, and M. Strongin, Phys. Rev. B **34**, 6759 (1986).

[7] M. El-Batanouny, D. R. Hamann, S. R. Chubb, and J. W. Davenport, Phys. Rev. B **27**, 2575 (1983).

[8] M. Sagurton, M. Strongin, F. Jona, and J. Colbert, Phys. Rev. B **28**, 4075 (1983).

[9] G. W. Graham, J. Vac. Sci. Technol. A **4**, 760 (1986).

[10] M. Pessa and O. Jylhä, Solid State Commun. **46**, 419 (1983).

[11] G. C. Smith, C. Norris, C. Binns, and H. A. Padmore, J. Phys. C **15**, 6481 (1982).

[12] X. Shen, D. J. Frankel, J. C. Hermanson, G. J. Lapeyre, and R. J. Smith, Phys. Rev. B **32**, 2120 (1985).

[13] B. Frick and K. Jacobi, Surf. Sci. **178**, 907 (1986).

[14] L. Q. Jiang, M. W. Ruckman, and M. Strongin, Phys. Rev. B **39**, 1564 (1989).

[15] V. Kumar and K. H. Bennemann, Phys. Rev. B **26**, 7004 (1982).

[16] M. El-Batanouny, M. Strongin, and G. P. Williams, Phys. Rev. B **27**, 4580 (1983).

[17] J. A. Rodriquez and D. W. Goodman, Science **257**, 897 (1992).

[18] R. E. Watson and L. H. Bennett, Phys. Rev. Lett. **43**, 1130 (1979).

[19] M. Strongin, M. El-Batanouny, and M. A. Pick, Phys. Rev. B **22**, 3126 (1980).

[20] Ch. Park, E. Bauer, and H. Poppa, Surf. Sci. **154**, 371 (1985).

[21] W. Schlenk and E. Bauer, Surf. Sci. **93**, 9 (1980).

[22] J. M. Heitzinger, S. C. Gebhard, D. H. Parker, and B. E. Koel, Surf. Sci. **260**, 151 (1992).

[23] A. Sellidj and B. E. Koel, Surf. Sci. **281**, 223 (1993).

[24] B. E. Koel, R. Smith, and P. J. Berlowitz, Surf. Sci. **231**, 325 (1990).

[25] A. Sellidj and B. E. Koel, Surf. Sci. **284**, 139 (1993).

[26] J. M. Heitzinger, A. Avoyan, and B. E. Koel, Surf. Sci. **294**, 251 (1993).

[27] D. L. Weissman-Wenocur, P. M. Stefan, B. B. Pate, M. L. Shek, I. Lindau, and W. E. Spicer, Phys. Rev. B **27**, 3308 (1983).

[28] M. A. van Hove, W. H. Weinberg, and C.-M. Chan, *Low Energy Electron Diffraction* (Springer-Verlag, New York, 1986).

[29] B. E. Koel, A. Sellidj, and M. T. Pafett, Phys. Rev. B **46**, 7846 (1992).

[30] J. A. Rodriguez, R. A. Campbell, and D. W. Goodman, J. Phys. Chem. **95**, 5716 (1991).

[31] X. Shen, D. J. Frankel, G. J. Lapeyre, and R. J. Smith, Phys. Rev. B **33**, 5372 (1986).

[32] R. G. Windham, M. E. Bartram, and B. E. Koel, J. Phys. Chem. **92**, 2862 (1988).

[33] M. P. Seah and W. A. Dench, Surf. Interf. Anal. **1**, 2 (1972); Surf. Sci. **44**, 29 (1979).

[34] N. E. Christensen and B. O. Seraphin, Phys. Rev. B **4**, 3321 (1971).

[35] K. A. Mills, R. F. Davis, S. D. Kevan, G. Thornton, and D. A. Shirley, Phys. Rev. B **22**, 581 (1980).

[36] The difference spectra shown in Fig. 3 were constructed by subtraction of the clean Au(111) spectrum from that of Pd-covered Au(111) after normalizing to the intensity of the Au-derived peak at −2.5 eV. Thus the difference spectra have intensity equal to zero at −2.5-eV binding energy.

[37] H. C. Potter and J. M. Blakeley, J. Vac. Sci. Technol. **12**, 635 (1975).

[38] J. E. Demuth, Surf. Sci. **65**, 369 (1977).

[39] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).

[40] X. Kiskinova *et al.* Surface Sci. **123**, 61 (1982).

[41] X. Guo and J. T. Yates, Jr., J. Chem. Phys. **90**, 6761 (1989).

[42] P. A. Redhead, Vacuum **12**, 203 (1962).

[43] T. Engel, J. Chem. Phys. **69**, 373 (1978).

[44] H. Conrad, G. Ertl, and J. Kuppers, Surf. Sci. **76**, 323 (1978).

[45] V. Kumar and K. H. Bennemann, Phys. Rev. B **28**, 3138 (1983).

[46] R. E. Watson, J. Hudis, and M. L. Perlman, Phys. Rev. B **4**, 4139 (1971).

[47] T. S. Chou, M. L. Perlman, and R. E. Watson, Phys. Rev. B **14**, 3248 (1976).

[48] T. K. Sham, M. L. Perlman, and R. E. Watson, Phys. Rev. B **9**, 539 (1979).

[49] G. K. Wertheim, R. L. Cohen, G. Crecelius, K. W. West, and J. Wernick, Phys. Rev. B **20**, 860 (1979).

[50] P. M. Th. M. van Attekum, G. K. Wertheim, G. Crecelius, K. W. West, and J. Wernick, Phys. Rev. B **22**, 3998 (1980).

[51] T. K. Sham, Solid State Commun. **64**, 1103 (1987).

[52] T. K. Sham, Y. M. Yiu, M. Kuhn, and K. H. Tan, Phys. Rev. B **41**, 11 881 (1990).

[53] T. K. Sham, Phys. Rev. B **31**, 1888 (1985); **31**, 1903 (1985).

[54] J. M. Heitzinger, S. C. Gebhard, and B. E. Koel, Surf. Sci. **275**, 209 (1992).

[55] G. W. Smith and E. Carter, J. Phys. Chem. **95**, 2327 (1991).