

Photoemission studies of ordered Pd overlayers on Au(111): Implications for CO chemisorption

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We present photoemission results for thin overlayers of Pd grown epitaxially on Au(111). The development of the Pd electronic structure near the Fermi energy is examined as a function of overlayer thickness. It is observed that the density of states at the Fermi energy is relatively small for the Pd monolayer and that the monolayer does not chemisorb CO at room temperature. We discuss the possible implications of this behavior for recent models of CO chemisorption.

I. INTRODUCTION

Modification of the physical and chemical properties of thin films and surfaces is of considerable interest in many areas of technology as well as basic science. It is well known that many transition metals, when prepared as epitaxial thin films, exhibit physical and/or chemical properties which differ considerably from those of the bulk material. Notable examples are the enhanced reactivity of ordered Au films on Pt(100),¹ the altered sticking coefficient for H on thin Pd films grown epitaxially on Nb(110),² and the increased paramagnetic susceptibility measured in Au-Pd-Au thin-film sandwiches.³ In the latter case the increased susceptibility was attributed to an increase in the Pd lattice constant due to the stretching of the epitaxial film by the outer Au which has a 4% larger lattice constant. The increased Pd spacing was thought to lead to an increase in the density of states at the Fermi energy E_F and thus to an enhanced magnetic susceptibility. However, photoemission measurements⁴ for a monolayer of Pd on Ag(111) with a lattice constant very close to that of Au showed a *decreased* electron density at E_F . A similar reduced density at E_F has been reported for Pd on Nb(110).^{5,6} Therefore, it is clear that more work is needed to relate the modified chemical properties to the altered electronic structure for these thin-film systems.

The purpose of the present paper is to report the results of a photoemission study of ordered Pd overlayers on the Au(111) surface. Our results for the electronic structure are consistent with the conclusion⁴ of a low electronic density at E_F for the Pd monolayer. Of greater interest, however, is the evidence we see for altered electronic structure in the Pd monolayer as manifested by the lack of CO chemisorption on the monolayer, in contrast to the surfaces of thicker Pd films which readily adsorb CO. We discuss our results in terms of recent cluster calculations for CO chemisorption,⁷ and related results for CO adsorption on thin Pd overlayers on Ta(110).⁸

II. EXPERIMENTAL PROCEDURES

The experiments were carried out in a stainless steel ultrahigh-vacuum (UHV) chamber which was fitted with

a single-pass cylindrical mirror analyzer (CMA) and coaxial electron gun for Auger-electron spectroscopy (AES) to monitor the amount of deposited Pd, a uv discharge lamp modeled after the design of Demuth,⁹ a double-pass CMA, which has been modified to collect either angle-integrated or angle-resolved photoemission spectra, a low-energy electron diffraction (LEED) system used to characterize the surface symmetry, an ion gun for sputter cleaning, and a quadrupole residual-gas analyzer (RGA). A special manipulator allowed the sample to be moved to the various working points. For photoemission measurements the sample normal was approximately 45° away from the CMA axis. The unpolarized light was then incident at an angle of approximately 45° from the surface normal, i.e., perpendicular to the CMA axis. The system was pumped by an ion pump, a turbomolecular pump, and a titanium sublimation pump; typical base pressures after bakeout at 150°C were below 1×10^{-10} Torr.

The substrate was a Au(111) single crystal, 3 mm thick and 6 mm in diameter, cut from a single-crystal Au rod, and prepared by chemical etching with cyanide at 50°C and *aqua regia* at room temperature. Laue x-ray backreflection patterns showed that the crystal was oriented to within $\pm 2^\circ$ of the (111) plane. The crystal was further cleaned *in situ* by several cycles of (1–3)-kV Ar⁺-ion bombardment and annealing. The sample rested on a button heater; various annealing temperatures between 700 and 850°C were used. Sample temperatures were measured with an optical pyrometer and a Chromel-Alumel thermocouple spot-welded onto a Ta mask which held the crystal on the button heater. After this cleaning procedure, Auger analysis showed that the carbon contamination was below the detection limits of AES. LEED showed a clean hexagonal (1×1) pattern.

The Pd was evaporated onto the Au(111) surface at room temperature, from small pieces of the metal (99.99% pure) resting inside an electrically heated tungsten basket. Before each evaporation, the basket was out-gassed by heating it to just below the sublimation temperature for Pd in UHV. The evaporation amounts of Pd were monitored with a water-cooled quartz-crystal oscillator (QCO). Because of possible inaccuracies in the relationship between frequency change for the QCO and actual film thickness on the substrate, mainly due to the diffi-

culty in accurately measuring the experimental geometry, the QCO results were only used as a rough indicator of film thickness and deposition rate. The actual coverage of Pd on the Au(111) surface was determined from the ratio of the peak-to-peak height of the Pd 330-eV Auger line to that of the Au 69-eV line. The mean free paths were taken to be 7 and 4 Å for the Pd and Au Auger electrons, respectively.¹⁰ Since escape depths for low-energy electrons in solids are not very well known, we estimate that our measured coverages may have an uncertainty of no more than 20%, based on a comparison of calculations for several different film thicknesses.

Since Au and Pd form a completely miscible alloy at all compositions,¹¹ we were very concerned about possible intermixing of the Pd adlayer with the substrate. To reduce this problem, no annealing of the overlayer was performed, and the substrate was held near room temperature during film deposition. From the Auger spectra, recorded after each evaporation, it was observed that the increase of the Pd 330-eV Auger line, and the decrease of the Au 69-eV line, were both initially linear functions of the evaporation time. Furthermore, at 1 monolayer (ML) Pd coverage, as determined from the attenuation of the Au 69-eV Auger line, the slope of the Pd Auger line decreased. This behavior is consistent with a layer-by-layer (Frank-van der Merwe) growth mode.¹² In addition, LEED observations after each evaporation indicated that ordered film growth of Pd on the Au(111) surface was taking place.

The experiments were performed following two different procedures. In the first procedure the Au(111) crystal was successively exposed to a certain amount of Pd, about 1 ML each time, and the changes in photoemission intensity as a function of Pd coverage were observed. In the second procedure, the clean Au(111) crystal was exposed to successively larger amounts of Pd, and after each evaporation and subsequent measurement, the surface was again cleaned by cycles of Ar⁺ bombardment and annealing. The results obtained from experiments following the two different procedures were essentially the same.

III. EXPERIMENTAL RESULTS

A. Pd on Au(111)

The system of Pd on Au lends itself naturally to studies of the state density near E_F . This is due mainly to the fact that the filled d bands of Au have an upper edge at an initial-state energy, $E_i \approx -2$ eV below the Fermi energy ($E_i = 0$ eV). The region of the photoemission spectrum, -2 eV $\leq E_i \leq E_F$, has a low emission intensity, associated with the emission from the filled sp bands of Au. This is evident in the bottom curves of Figs. 1 and 2, which show the valence-band portion of the emission intensity from clean Au(111) for incident photon energies of 21.2 and 40.8 eV, respectively. These curves are plotted as a function of initial-state energy below the Fermi energy, $E_F = 0$. The region of low emission intensity near E_F serves as a window which allows us to monitor the development of the overlayer states near E_F with relatively little interference from the Au d bands. The corre-

sponding window for Pd on Ag is nearly 4 eV wide.⁴

In Figs. 1 and 2 we show the valence-band photoemission spectra for increasing coverages of the Pd overlayer on Au(111). It is apparent that the effect of Pd is to initially add structure to the curves just above the Au d bands. With increasing Pd coverage the emission intensity increases more notably near E_F . At the same time both sets of data show the decrease in emission from the Au d bands, centered near -3.5 and -6.2 eV, as the substrate is covered with Pd. The greater surface sensitivity at $h\nu = 40.8$ eV (Fig. 2) is also noticeable in these figures in that 2.8 ML of Pd is nearly enough to suppress substrate d -band emission for $h\nu = 40.8$ eV, while the Au d bands at -6.2 eV are still visible even for 5.6 ML of Pd with $h\nu = 21.2$ eV.

A closer examination of the Pd d -band development near E_F shows that the emission intensity for initial energies between -1.0 and -1.5 eV grows rapidly, nearly saturating by 2 ML coverage, while the emission intensity near E_F grows steadily from a relatively low value at 1 ML to the bulk emission intensity for about 5 ML film thickness. This evolution of the features in the "window" region is quite evident in the sequential difference curves plotted in Figs. 3 and 4 for $h\nu = 21.2$ and 40.8 eV, respectively. These curves are formed by subtracting from the spectrum for the most recent evaporation the spectrum for the previous evaporation, and thus show the effects associated with the addition of the outermost Pd atoms. We

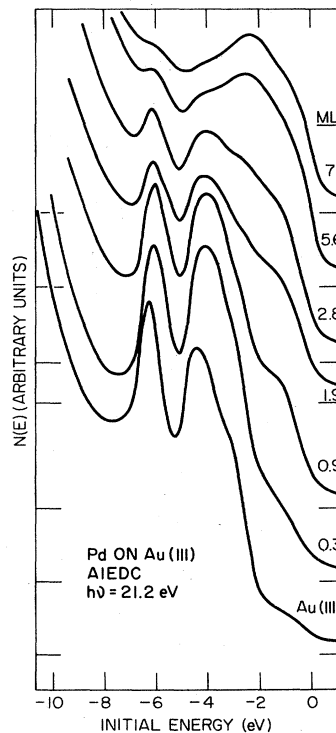


FIG. 1. Valence-band portion of the CMA angle-integrated photoemission spectra for Pd overlayers on Au(111), $h\nu = 21.2$ eV. The curves are plotted as a function of initial-state energy below the Fermi energy. Overlayer thickness is indicated at right.

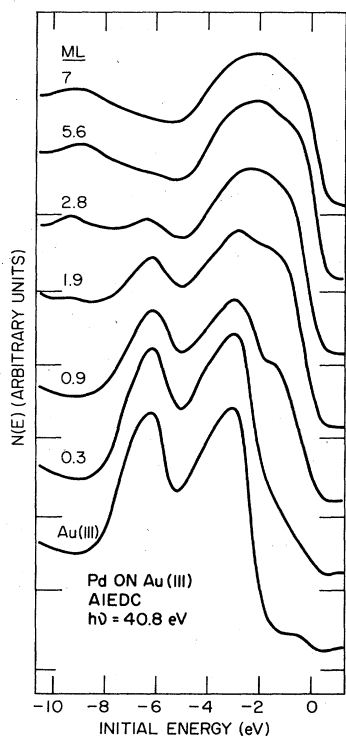


FIG. 2. Valence-band portion of the CMA angle-integrated spectra for Pd overlayers on Au(111), $h\nu=40.8$ eV. Overlayer thickness is indicated at left.

see clearly a relatively narrow peak centered at $E_i \approx -1.6$ eV for 0.3 ML Pd. With increasing Pd coverage, a broadened feature is observed, centered near -1.0 eV, at ≈ 2 ML. With nearly 3 ML of Pd on the Au surface, the principle difference feature is a peak very near E_F at -0.3 eV. The attenuation of the Au d bands is also apparent in these figures as negative-going peaks with sequentially decreasing amplitude.

The work function of the surface, as determined from the energy width of our photoemission spectra, was observed to increase abruptly with the smallest amount of deposited Pd. We obtained a value of 4.6 eV for the clean Au(111) surface. A deposition of only 0.3 ML Pd raised the work function to 5.2 eV. We then observed a slow increase of work function, to a value of 5.4 eV for 5 ML Pd. Demuth¹³ has reported a work function of 5.6 eV for Pd(111). Attempts to regain the work-function value for clean Au by sputter-cleaning the surface were unsuccessful. Although the Pd concentration was reduced to much less than 1% of the Au as measured by AES, we could only reduce the work function to a value of 5.2 eV, the value measured for our lowest Pd coverages. A chemical etch of the crystal surface restored the work function to 4.6 eV, and the abrupt increase in work function was again observed in subsequent experiments. Our value of 4.6 eV for the work function of Au(111) is well below the typical value of 5.3 eV reported for polycrystalline Au.¹⁴

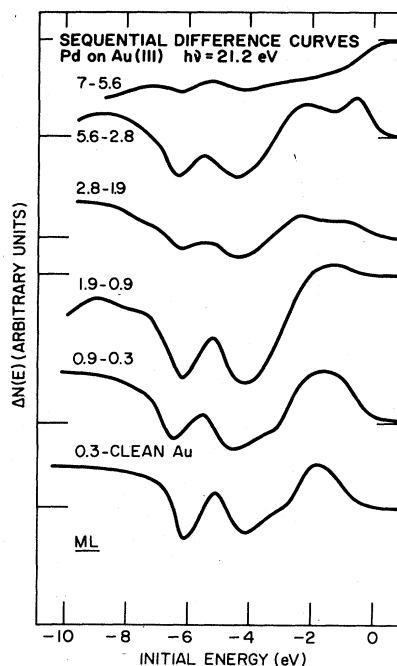


FIG. 3. Sequential difference curves obtained by subtracting the photoemission spectra for the thinner film from that of the thicker film. Measured film thickness is shown at the left; $h\nu=21.2$ eV. Horizontal lines indicate the zero for each subtraction.

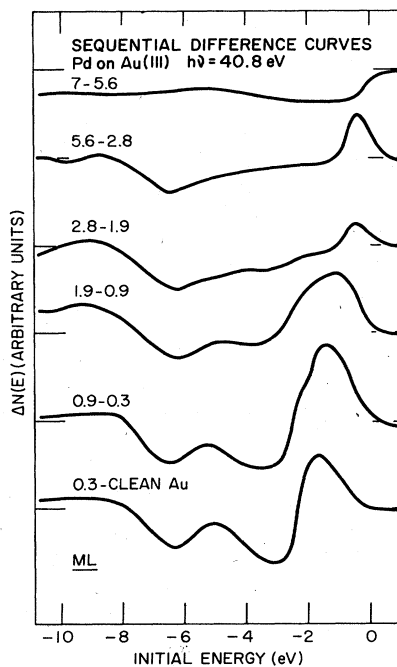


FIG. 4. Sequential difference curves obtained by subtracting the photoemission spectra for the thinner film from that of the thicker film. Measured film thickness is shown at the left; $h\nu=40.8$ eV. Horizontal lines indicate the zero for each subtraction.

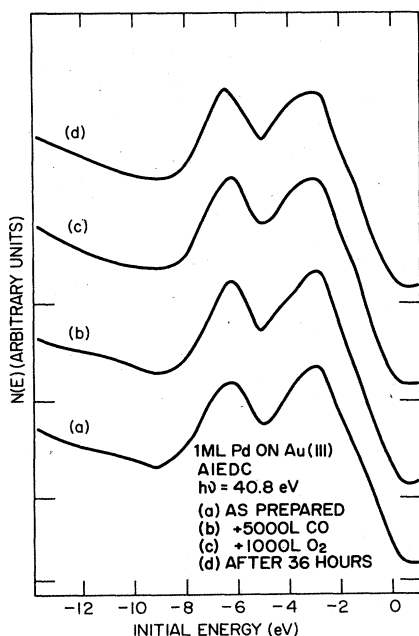


FIG. 5. Photoemission spectra ($h\nu=40.8$ eV) for the valence-band region of a 1-ML Pd film: (a) immediately after film deposition, (b) after additional exposure to 5000 L CO, (c) after additional exposure to 1000 L O_2 , and (d) after total of 36 h in the UHV chamber at 2×10^{-10} Torr.

B. Adsorption of CO on thin Pd layers

The photoemission spectra for monolayer thickness films were observed to remain unchanged for times in excess of 36 h in the residual-gas environment at $\leq 2 \times 10^{-10}$ Torr as shown in Fig. 5. In contrast, all the spectra for thicker films showed evidence of CO contamination immediately after deposition, as shown in the lower curve of Fig. 6. The two peaks centered at -10.8 and -7.8 eV are attributed, respectively, to the 4σ and 1π plus 5σ molecular orbitals of CO.¹⁵ Apparently, the surface contamination occurred during film deposition, at which time the chamber pressure was $\approx 1 \times 10^{-9}$ Torr, due to evolution of H_2 and CO during heating of the evaporant and basket. Unlike the monolayer films, the thicker films were quite sensitive to the residual gas following evaporation. After 4 h at 2×10^{-10} Torr the double CO peaks on the thicker films evolved into a single peak, centered at -9.4 eV. As pointed out below, a similar single peak was observed when the CO-covered surface was exposed to O_2 . These surfaces were not cleaned by thermal desorption because of the potential for considerable diffusion and loss of the overlayer structure.

To further explore the adsorption properties of the thin Pd films, we exposed the surfaces to various amounts of CO and/or O_2 . In Fig. 6 curve (a) is the photoemission spectrum for a 3-ML Pd film recorded immediately after deposition. The characteristic CO features are present. Additional exposure to CO had a negligible effect on this spectrum. Exposure to O_2 caused the CO peaks to gradually evolve into a single peak at -9.4 eV as shown in

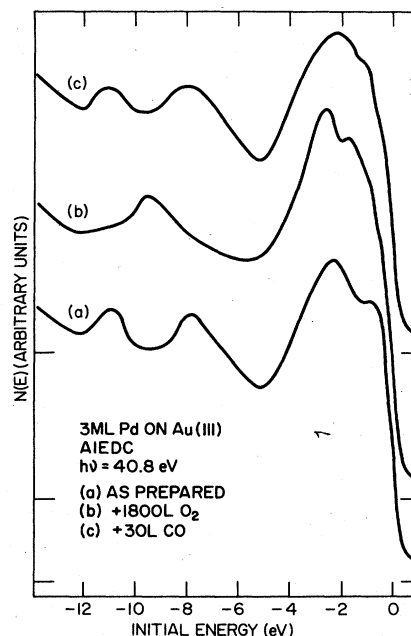


FIG. 6. Photoemission spectra ($h\nu=40.8$ eV) for the valence-band region of a 3-ML Pd film: (a) immediately after film deposition, (b) after additional exposure to 1800 L O_2 , and (c) after additional exposure to 30 L CO.

curve (b). Subsequent exposure to 30 L of CO ($1L=1$ langmuir $= 10^{-6}$ Torr sec) caused the spectra to evolve back to one characteristic of chemisorbed CO as shown in curve (c). This process was reversible and could be repeated for several cycles. We note, however, that the emission near E_F which is reduced by the initial oxygen exposure, did not return with subsequent CO exposures. In contrast to the thick-film behavior just mentioned, a 1-ML Pd film showed no CO- or O_2 -induced features when subjected to similar gas exposures, as demonstrated in Fig. 5. It appears then that the monolayer of Pd is quite inert to CO chemisorption, in marked contrast to the thick-film behavior.

IV. DISCUSSION

A. Pd on Au(111)

There are a few points about our observations which need further discussion. First, at submonolayer coverages we have almost no Pd contribution near E_F , as shown in the difference curves of Figs. 3 and 4. We assign the relatively narrow feature at -1.6 eV for 0.3 ML to atomic-like Pd d states. This assignment is consistent with results for dilute Pd alloys which show a similar feature,¹⁶ and with photoemission studies for thin Au overlayers on Pd(111).¹⁷ In the latter experiments small amounts of Au, up to 1 ML coverage, caused certain Pd structures near E_F to sharpen up, and structure at -1.5 eV was noticeably enhanced. The sharpness or narrowing of spectral

features near E_F was attributed to an increase in atomic-like character for the Pd surface atoms as the Au sp electrons began to screen the surface atoms and to reduce the $d-d$ interaction. Our results nicely complement those of Spicer *et al.* in that we are able to observe this presumed atomiclike character for the dispersed Pd atoms at submonolayer coverages. Unfortunately, we cannot see clearly any interface features at initial-state energies below -2 eV since the Au d bands tend to dominate the spectra in this regime.

A second major point about our results is that for one monolayer of Pd on Au(111) the Pd d states appear to be filled and located below E_F . In this respect, the supported monolayer resembles a noble metal like Cu, with the filled d bands just below E_F , but higher than the Au d bands. These results are in many ways similar to those for Pd on Ag(111),⁴ and for Pd on Nb(110).^{5,6} However, this similarity *would not* be predicted based on charge-transfer arguments, since the electronegativity on Pauling's scale is 2.4 for Au and 2.2 for Pd. Thus, we would expect charge transfer from Pd to Au. Charge transfer to the Pd overlayer is predicted for the Pd-Ag and Pd-Nb systems since the electronegativities of Nb and Ag are 1.6 and 1.9, respectively, both less than that of Pd. We also note that in the analogous bilayer system of Ni on Cu(001) the electronegativity differences of 0.1 predict a small charge transfer from Ni (1.8) to Cu (1.9), but slab calculations¹⁸ show negligible interlayer charge transfer. There is, however, some intralayer sp -to- d charge transfer in the surface Ni layer, which partially fills the d -band density of states.

We observe an abrupt work-function increase with Pd coverage, from 4.6 eV for clean Au(111) to 5.2 eV for 0.3 ML of Pd. The work function is then fairly constant up to 3 ML of Pd, and increases slightly to 5.4 eV for thicker films. The work-function increase is consistent with charge transfer to the Pd overlayer; however, the abrupt increase at very low coverages is in marked contrast to the gradual work-function increase observed for Pd on Ag(111).⁴ We believe that these surprising results for Pd on Au(111) call for further theoretical study of this bilayer system.

B. Chemisorption properties of thin Pd films

The altered reactivity of thin Pd films, and other metallic films, is usually attributed to changes in the d -band density of states near E_F . For example, the electronic structure of a Pd monolayer on Nb(110) was shown to have a reduced d -band density at E_F .^{5,6} This fact was used to explain the reduced sticking coefficient for H_2 on thin Pd films² and the lack of CO adsorption for a monolayer of Pd on Ta(110) and Nb(110).⁸ LEED and UPS studies¹⁹ showed that the structural phase transition for these Pd films, from commensurate Pd*(110) to incommensurate Pd(111), precedes the onset of CO chemisorption, and that the electronic structure of the film does not change much during the structural transition. As the Pd coverage is increased in the incommensurate phase, the density of states near E_F increases and CO chemisorption begins. Our results for Pd on Au(111) demonstrate the in-

ert behavior of the Pd(111) monolayer, even for submonolayer coverage, without the complication of the structural phase transition inherent to the Pd-Nb system.

The inert behavior with respect to CO chemisorption on the Pd monolayer can be understood crudely in at least two ways. Following the argument of Blyholder,²⁰ CO bonding is comprised of two parts: (1) charge donation from the 5σ lone-pair CO orbital to unoccupied metallic acceptor states of σ symmetry just above E_F , and (2) charge back-donation from filled metallic π -symmetry states to the empty antibonding 2π orbital localized on the CO molecule. If the Pd d states are filled and pulled below E_F due to adsorption on Au, we not only reduce the number of available $d\sigma$ -symmetry holes at E_F , but also increase the energy gap between the $d\pi$ -symmetry states and the empty 2π molecular orbital. Both factors reduce the charge transfer and probably reduce the bond energy. The relative contributions of σ and π charge donation to the CO-metal bond has been addressed recently in a series of papers by Bagus *et al.*⁷ These authors conclude, based on results of cluster calculations, that the π donation from substrate to molecule is the dominant bonding contribution and that σ donation is of lesser importance, and may in some cases lead to a repulsive contribution to the CO-metal interaction.

Alternatively, one can view the CO adsorption process in terms of the sticking coefficient and ask how easily the surface can adjust to the incoming molecule; that is, we must excite electrons near E_F to empty states just above E_F .²¹ This process might be enhanced if the local surface density of states at E_F is high; and reduced, if the density of states is somehow lowered. Such a reduction may explain the inert behavior of the Pd monolayer where the d -band density of states at E_F is apparently much less than that for bulk Pd films. Again, an analogy with the electronic structure of Cu is suggested, and one might expect the Au-supported Pd monolayer to exhibit the weak chemisorption characteristics seen for CO on Cu or CO on tantalum-supported Pd thin films.²²

Finally, we note that the evolution of the CO molecular orbitals from a single peak at -9.4 eV, as seen in Fig. 6, was observed previously for adsorption of CO on a NO-covered Pd(110) surface.²³ In our work, however, there is no known source of nitrogen, nor is any nitrogen-containing molecule seen with the quadrupole gas analyzer. Furthermore, in our case this displacive-type chemisorption was reversible for O_2 and CO exposures as seen in Fig. 6. We are investigating further this interesting reversible mechanism involving CO and O_2 coadsorption and the results will be reported elsewhere.

V. SUMMARY

We have measured the angle-integrated photoemission spectra for ordered overlayers of Pd on Au(111) as a function of increasing Pd coverage. Submonolayer films exhibit a photoemission peak at -1.6 eV which we assign to atomiclike Pd d levels associated with dispersed Pd atoms. There is no significant emission intensity at the Fermi energy for the Pd monolayer, but the emission near E_F does show a monotonic increase as the bulk Pd electronic structure develops. The monolayer films appear to

be inert to CO chemisorption, while thicker Pd films exhibit the usual photoemission peaks for chemisorbed CO. We associate the lack of CO chemisorption on the Pd monolayer with the redistribution of the manifold of Pd *d* states.

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