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Adsorption of CO on thin Pd overlayers on Nb(110) and Ta(110)

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It is found that CO does not chemisorb at room temperature on Ta(110) covered by a monolayer of Pd, whether or not the Pd is in a commensurate or incommensurate structure. Weak chemisorption occurs on this overlayer at liquid-nitrogen temperature. As further layers of Pd are deposited and the surface electronic structure becomes characteristic of Pd(111) (there is an increase of states near E_F), the chemisorption of CO increases.

In the past two years the study of the interaction of metal overlayers with molecules has had increased interest.[1–6] In our own work we have been particularly interested in the modification of the electronic properties of the overlayer due to the hybridization of the orbitals of the overlayer with the metal underneath,[7] and recent theoretical work has also addressed this particular problem.[8,9] A subject of further interest is the structure and structural transition in the overlayers and whether this affects the electronic properties.[10–12] In fact, the whole question of how the electronic properties return to the bulk metal as the overlayers become thicker, and how the chemical reactivity changes, is a problem of great interest and is discussed in this paper.

In previous work it was found that Pd on Nb(110),[10,11] and also on Ta(110),[12] goes down in a commensurate layer, and that the density of states on this thin Pd layer shows a narrow *d* band about 2 eV below E_F, with a corresponding decrease in Pd *d* states at E_F. Through hydrogen uptake experiments[13] and work function and photoemission measurements,[14] it appears that the low uptake rate through this layer is due to the low dissociation rate of hydrogen on this surface, in much the same fashion as for hydrogen on copper or silver. As the second layer and subsequent layers were added, the uptake rate increased. In a recent study the electronic structure was investigated as the Pd overlayer went through a structural transition from a commensurate to an incommensurate overlayer.[11,12] No major change was found in the electronic structure as this happened, although some additional states started to appear about ≈ 1–2 eV below E_F. The Pd electronic structure then changed continuously, with states appearing at E_F, as additional layers were added.

In this work we investigate the chemisorption of CO in detail as one goes through this structural transition for the case of Pd on Ta(110). Results for CO on commensurate layers of Pd-Ta(110) are also presented at room- and liquid-nitrogen temperatures, and some brief discussion is given of previous unpublished work on Pd layers on Nb(110). The details of the growth of Pd on Ta is similar in almost all aspects to previous work on Nb,[7,10,11] and the details will be described elsewhere.[12]

These experiments were carried out using a bakable ultra-high vacuum (UHV) system in which ultimate pressures of less than 5×10^{-10} Torr could be achieved. The system was equipped with a low-pressure He plasma lamp and a conventional double-pass cylindrical mirror analyzer (CMA).

Tantalum and niobium samples were prepared from Marz-grade (Materials Research Corp.) polycrystalline foils 0.002 in. thick. Impurities such as carbon and sulfur were removed by annealing in oxygen. Surface oxides and sulfur were removed by repeated flash heating to ≈ 2500 K. Single-crystal specimens with (110) orientation suitable for photoelectron spectroscopy were created by briefly heating the foil to the melting point for subsequent recrystallization. Tantalum and niobium crystals grown in this fashion were readily visible to the experimenter and were at least 1–2 mm in size.

Resistively heated tungsten baskets with pieces of Marz-grade Pd foil were used as vapor sources to evaporate high-purity Pd films. The base pressure rose to 7×10^{-9} Torr during Pd evaporations. During CO exposures the chamber was filled with CO up to a partial pressure of 5×10^{-8} Torr.

Figure 1 shows major features of the data. In Fig. 1(a) the data for clean Pd overlayers on Ta are shown, and in Fig. 1(b) the effect of CO on these different coverage layers is seen. The absence of chemisorbed CO is evident on the commensurate layer where $\bar{n}=1$. Furthermore, these data show dissociative chemisorption of CO on clean Ta and low coverages of Pd on Ta ($\bar{n}<1$), with peaks at -4 and -6 eV. As thicker Pd overlayers ($\bar{n}>1$) are built up the peaks characteristic of nondissociative CO chemisorption on Pd are seen at -8 and -12 eV. At this photon energy the -12-eV peak is difficult to see because it is obscured by secondary photoelectrons. Spectra taken at greater photon energy clearly show the -12-eV peak.

In Fig. 2, a major result of this paper is summarized, *namely, the absence of CO chemisorption on a monolayer of Pd on Ta whether the Pd is in the commensurate or incommensurate structure.* Figure 2 shows the relative CO coverage after exposures of 10 and 21 L (1 L$=10^{-6}$ Torr sec) of CO as a function of Pd coverage relative to the coverage on a clean Ta(110) surface, as obtained from the height of the oxygen 2*p* feature at -6 eV for Pd coverages less than one layer

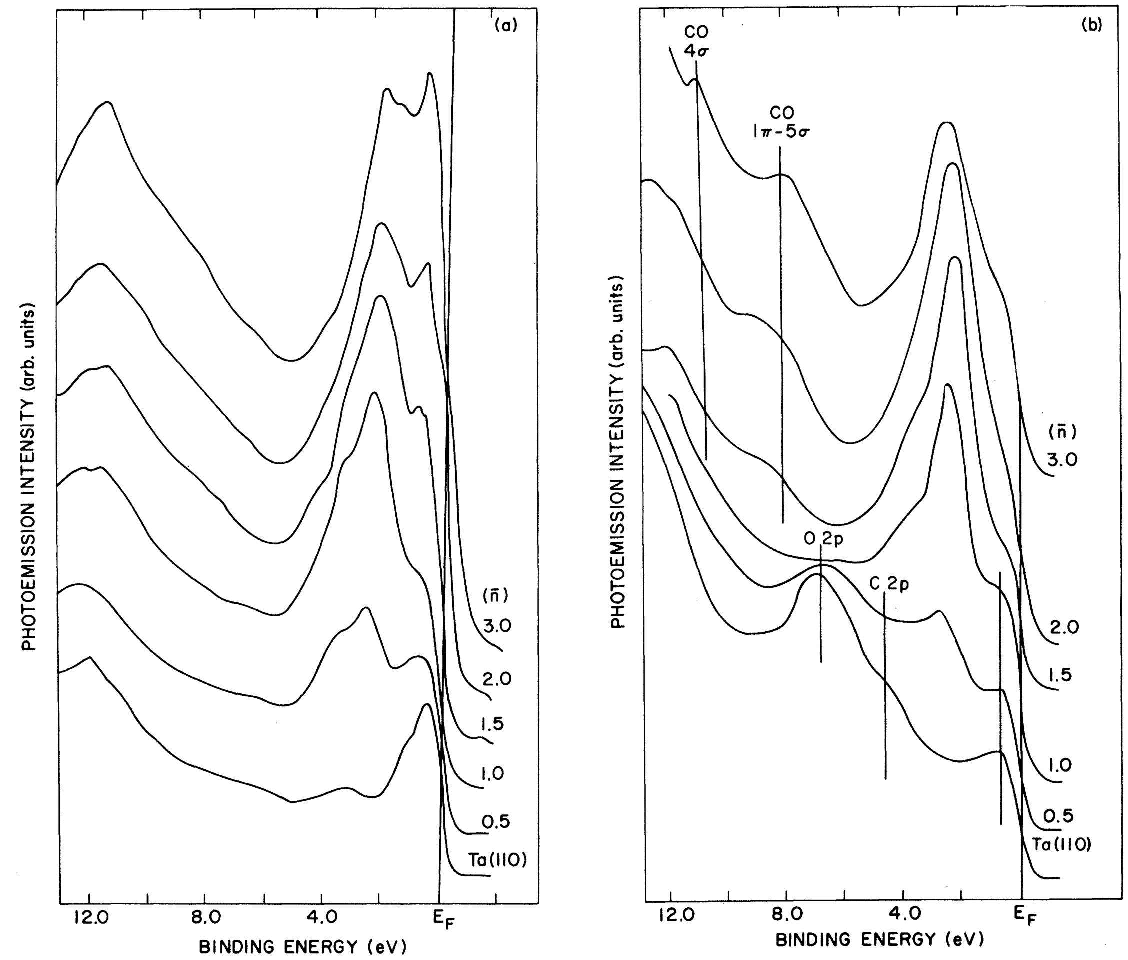

FIG. 1. (a) Angle-integrated photoemission spectra obtained from a Ta(110) surface for various coverages of Pd. $\bar{n}$ is the estimated film thickness or coverage; a monolayer equals 1.0. (b) Angle-integrated photoemission spectra for the surfaces shown in (a) after exposure to 21 L of CO as measured at the vacuum gauge.

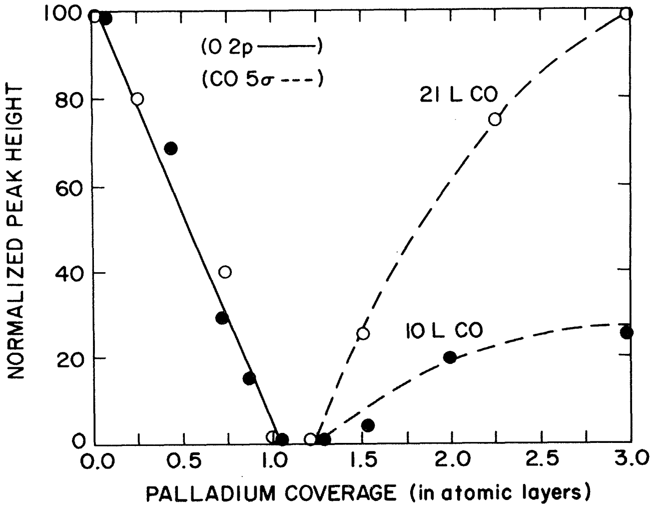

FIG. 2. Coverage of CO on Pd overlayers on Ta(110) after exposure to 10 L (●) or 21 L (○) of CO gas as measured at the vacuum gauge. Approximate CO coverage was determined using the height of the CO-derived photoemission features. (6-eV peak of the O 2p orbital for dissociative chemisorption, and 8-eV peak of the 5σ CO orbital for nondissociative chemisorption.)

and the CO 5σ-1π molecular feature at -8 eV for Pd coverage above one layer. This figure shows that the CO coverage varies (decreases) almost linearly with Pd coverage up to a monolayer. Earlier low-energy-electron diffraction (LEED) experiments strongly suggested that Pd in the first layer grows by forming two-dimensional islands.[11] The results here strongly suggest that Pd on Ta(110), whether as islands or a monolayer, is inert to CO chemisorption. Therefore the reduction in CO coverage is due entirely to a reduction of the area of the Ta(110) surface.

It should be mentioned that the thickness scale of Figs. 1 and 2 was determined by depositing successive amounts of Pd for given times. The value at one layer was determined from photoemission measurements, and by calibration from Auger intensities on separate runs. Monolayer coverages can also be achieved by heating a thicker Pd layer to about 1000 °C,[11,12] which leaves a stable surface layer with the same LEED pattern, and basically the same photoemission pattern (although somewhat more intense and sharper), as the deposited layer. Furthermore, as for the deposited layer, this layer does not chemisorb CO at room temparature. We mention that the Auger intensities for the heated layer yield about 20% less Pd at a monolayer thickness. This is most likely because the incommensurate phase first appears in the deposited overlayer before the whole surface is covered, at a thickness of about 0.8 monolayers, due to the formation of some incommensurate Pd(111) islands, as some Pd statistically goes into the second layer and causes the commensurate to incommensurate transition to occur in some regions. Hence by the time the whole Ta surface is covered with Pd, which includes mostly the commensurate layer plus some islands of Pd(111) which statistically form, about 1.2 equivalent layers of commensurate Pd are on the Ta surface. Further deposition now causes the incommensurate phase to finally cover the whole surface.

Addition of Pd resulting in Pd coverages beyond 1.2–1.4 layers produced a surface that began to molecularly chemisorb CO. The amount of CO coverage obtained depended on the partial pressure and total CO exposure. We found that exposures of at least 21 L were necessary in order to saturate the surface with CO. Our data do not permit us to rule out the possibility that increased surface roughness causes the enhancement in CO uptake. However, LEED patterns of Pd overlayers with Pd exposures sufficient to produce two- and three-layer overlayers were quite sharp and nearly indistinguishable from LEED patterns of atomically smooth Pd(111) single crystals cleaned by sputtering.

Previous work on CO chemisorption on Pd on Nb(110) yielded similar results, i.e., no chemisorption at room temperature and chemisorption at low temperature.[15] However, this system was never studied in the incommensurate phase. We would expect results similar to the present study for the Pd on Nb case.

The major conclusion of this work is that CO does not chemisorb at room temperature on a single Pd overlayer on Ta, whether the Pd is in the commensurate phase or the incommensurate phase. At lower temperatures weak chemisorption occurs. The insensitivity to the transition from the commensurate to incommensurate layer is expected from work on the electronic structure of the overlayers[8,9] where the additional Pd atoms which form the incommensurate layer are not expected to greatly alter the electronic structure. Furthermore, detailed photoemission measurements on both Pd-Nb and Pd-Ta show that there is no dramatic change in the *d* bands when the commensurate to incommensurate transition occurs. Since the incommensurate layer has the Pd structure, these results show that geometrical structure is not crucial to CO chemisorption in this case.

As the second and subsequent layers are deposited detailed photoemission results show a buildup of *d* states near E_F, and it is in this regime that CO chemisorption starts to increase to a value characteristic of bulk Pd. Clearly the single-layer case, because of hybridization to the substrate, behaves very much as a noble metal such as copper or silver with respect to CO chemisorption and hydrogen dissociation.

Drastic reduction of CO coverage on a late transition-metal overlayer on an early transition-metal substrate has been reported by Prigge, Schlerk, and Bauer[16] for Pd monolayers on W(110). Poppa and Soria[17] also report that CO coverage is also reduced on thicker (3–4 monolayers) Pd layers on Mo(110) subjected to heat treatments of 650 K or greater. In both cases the authors note that Pd overlayers on W and Mo are metastable in the sense that Pd agglomorates on top of a Pd monolayer on the Mo or W substrate. CO coverage on Pd/Mo was reduced by decreasing the surface roughness. However, in no case was the CO coverage on Pd layers reduced below the values known for smooth single-crystal Pd(111). Only on the Pd monolayer with its unusual electronic properties and lower work function was CO coverage reduced to zero.

The implication of this present work is that the electronic properties of the overlayers play a major role. In other work,[16] edge effects have also been suggested and cannot be conclusively ruled out in this work. However, we find the correlations with the changes in the electronic features to be compelling. We have emphasized the simple correlation to states near E_F, but clearly the center of gravity of the Pd *d* bands changes and other features in the electronic structure may be crucial in explaining these observations.

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