

Monolayer Metal Films on Metallic Surfaces: Correlation between Electronic Structure and Molecular Chemisorption

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Received January 3, 1994

Bimetallic alloys or compounds have been used in selected heterogeneous catalysts.¹ A typical catalyst of this type usually has the bimetallic phase dispersed as small particles in a matrix or over a support material.² An important theme of much of the research in this area is the relationship between the electronic structure of the bimetallic component and the catalytic properties.³ Chemists, materials scientists, and condensed matter physicists have used many techniques and approaches to improve our understanding of this phenomenon. For example, some investigators have studied the bimetallic catalysts or the bimetallic particles themselves,^{3,4} whereas other workers have examined model thin film systems composed of the same metals.⁵ From such work on bimetallic systems, it is now known that trends in the chemical reactivity can be correlated with variables like d-band occupancy and electronegativity.⁶ Consequently, some workers have advanced the idea that charge transfer from one metallic element to another is responsible for the behavior of bimetallic systems.⁷ This Account discusses some spectroscopic and theoretical studies of thin late transition metal overlayers (i.e., Pd) on early transition metal surfaces (i.e., Nb or Ta) done at Brookhaven during the 1980s. This work sheds light on how the modification of electronic structure of metal monolayer thick metal films impacts the chemical properties of the films. In contrast to recent claims by other workers,⁸ our work indicates that charge transfer between the overlayer and the substrate is not the dominant factor in modifying the properties of the supported metal overlayer. This Account is not intended to be an exhaustive review of the large body of work in this field. The following discussion focuses on late-on-early transition metal bimetallic systems, such as Pd/Ta or Pd/Nb, because the magnitude of the change in carbon monoxide adsorption, often used as a measure of surface chemical activity, is one of the largest known.⁹ Since our initial studies of such palladium monolayers over a decade ago,¹⁰⁻¹⁵ our group has performed additional experiments on a number of similar bimetallic systems

(Pt, Ni, Cu, Ag, Au, and Rh on Ta(110))¹⁶⁻¹⁸ and a related bimetallic system (Rh/Mo).¹⁹ Inverse photoemission was used by Pan et al. to study changes in the unoccupied electronic structure of Pd-covered niobium surfaces.²⁰ Theoretical work has also been undertaken by Weinert et al.²¹ to study the energetics and physical properties of bimetallic films, compounds and multilayers. Koel et al.^{21,22} have confirmed the original experiments¹⁰⁻¹⁵ and have used additional techniques like high-resolution electron energy loss spectroscopy (HREELS), temperature programmed desorption (TPD) spectroscopy, and Fourier transform infrared (FTIR) spectroscopy to study the properties of carbon monoxide adsorbed on Pd/Ta(110). The authors have certainly not been alone in this active area of chemical physics research, and many related bimetallic thin film systems²⁴⁻³⁶ have been studied.

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Myron Strongin was born in Brooklyn, NY in 1936. He graduated from Rensselaer Polytechnic Institute in 1956 and received his Ph.D. degree from Yale in 1962. He worked at MIT Lincoln Laboratories before coming in 1963 to Brookhaven, where he is currently a Senior Physicist. His research interests include superconductivity and low-temperature physics, and with the advent of synchrotron sources, he has been interested in using vacuum ultraviolet spectroscopy to characterize metals and metal/overlayer systems and their interaction with gases.

Several good reviews^{5,37-39} of such work have been published.

The first part of this Account summarizes our studies of CO adsorption on thin metal overlayers and shows that changes in the strength of the CO-metal interaction can be correlated to systematic changes in the valence electronic structure. The next section discusses the measurements of valence photoelectron spectra, core level binding energies, and work functions and illustrates the limits of these experiments in providing an accurate measure of the charge redistribution that occurs during the hybridization of overlayer and substrate valence states. Finally we will show how the experiments discussed in the first two parts can be explained using a widely accepted model for surface chemical bonding.

Carbon Monoxide Adsorption on Supported Metal Monolayers

Two of the most important discoveries from our initial work on tantalum- or niobium-supported Pd monolayers were (1) a drastic reduction in hydrogen uptake through Pd monolayers¹¹ and (2) observation of a sharp reduction in the sticking coefficient⁴⁰ for CO on Nb- or Ta-supported Pd monolayers.¹⁴ For the case of CO on Pd/Ta(110) or Pd/Nb(110), it was found that CO does not *chemisorb* on commensurate or incommensurate Ta(110)-supported or Nb(110)-supported Pd monolayers at 300 K, whereas a monolayer of CO *chemisorbs* on single-crystal Pd(111) surfaces at the same temperature. Since the publication of our earlier work on palladium monolayers, we have found that Ni and Pt monolayers deposited on Nb(110) or Rh monolayers on Mo(110) substrates also have reduced CO sticking coefficients at 300 K. This interesting property of late transition metal monolayers on Nb(110), Ta(110), or Mo(110) substrates at 300 K is summarized in Figure 1, where the normalized intensity of CO-related or CO dissociation product photoemission features for equivalent 20-L (langmuir) (1 L = 10⁻⁶ Torr) CO exposures is shown as a function of the metal overlayer coverage. In each case plotted, there is less CO or there are fewer CO dissociation products⁴¹ on the surface near monolayer metal coverage. In the case of uncovered Mo(110), Nb(110), or Ta(110) surfaces, CO chemisorbs dissociatively (i.e., the molecule breaks into adsorbed carbon and oxygen atoms). When late transition metal films are grown on these surfaces, the amount of carbon or oxygen, for equal exposures of CO, is found to decrease

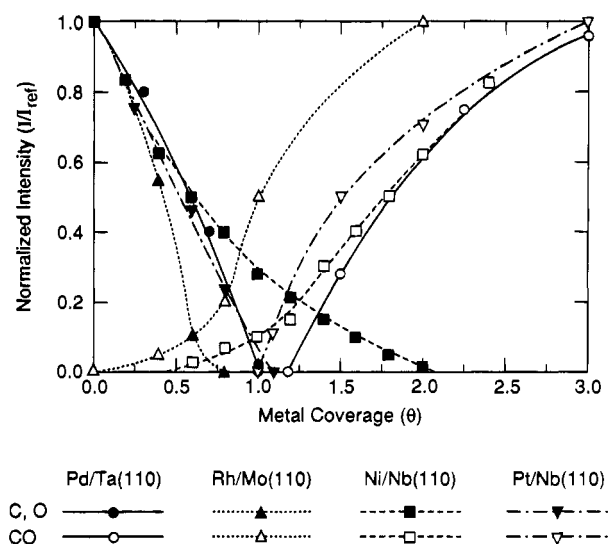


Figure 1. Normalized (I/I_{ref}) intensity variations of photoelectron features attributed to C + O (solid symbols) or molecular CO (open symbols) as a function of metal overlayer coverage for a variety of bimetallic systems. For Pd/Ta(110) and Pt/Nb(110), the virtual absence of photoelectron emission from CO or its dissociation products on complete monolayers argues for negligibly small sticking at 300 K. All the bimetallic systems studied show a significant reduction in CO adsorption when the metal overlayers are of atomic thickness.

with increasing metal coverage. For complete Pd or Pt monolayers on Ta(110) or Nb(110), respectively, there is no detectable CO, C, or O on the surface as judged by the absence of the photoemission features. For other systems like Ni/Nb(110) or Rh/Mo(110), it was found that the carbon or oxygen features persisted beyond the deposition of sufficient amounts of metal to cover the surface. For Pd and Pt on Nb(110) or Ta(110), features associated with molecular CO were absent at 300 K, whereas molecular CO features were also detected on Ni or Rh films on Nb(110) or Rh/Mo(110) for submonolayer coverage. The data shown in Figure 1 strongly suggests that the sticking coefficient for CO (300 K) on Pd or Pt (islands or monolayers) is negligibly small. In addition this data also shows that the sticking coefficients for Ni and Rh monolayers or 2-D islands are significantly smaller than on comparable clean Rh(111) or Ni(111) surfaces at room temperature.

In our initial work, we suggested that *the negligible sticking of CO was due to a reduction in the adsorption energy of CO on those surfaces*. The evidence that the metal-CO bond is weaker is 2-fold; (1) CO is desorbed from the surface at lower temperatures; and (2) the appearance and binding energies of the CO photoemission features (from CO adsorbed on Pd monolayers at liquid nitrogen temperatures) are more like those of CO on Cu(111),⁴¹ which forms a weaker surface bond than CO on Ni(111),⁴² which resembles Pd(111) and forms a significantly stronger surface bond. Furthermore, our own work also shows changes in the screening of the adsorbate photoelectron features, indicating weak adsorption for CO adsorbed at low temperatures.¹⁵ The adsorption of CO on Pd/Ta(110) has been studied in detail by Koel and co-workers^{9,22,23} and by Berlowitz and Goodman.²⁵ Koel's group found that the desorption temperature for CO on Pd/Ta(110) was significantly smaller than on Pd-

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(111). For Pd/Ta(110), the heat of adsorption of CO, as judged by temperature programmed desorption (TPD), is lowered by 15 kcal/mol²² compared to Pd(111). Goodman's extensive work in this area also shows that this reduction in the heat of adsorption exists for many other systems. In addition, Sellidj and Koel^{22,23} have studied the HREELS features related to the CO molecule and found evidence supporting a weaker Pd-CO interaction for CO on Ta-supported Pd monolayers than on Pd(111). In particular, they find that the CO stretch frequency decreases from 2040 cm⁻¹ to 1940 cm⁻¹ in going from 1 ML of Pd/Ta(110) to Pd(111)-like multilayers. Similar phenomena in FTIR spectra have also been reported by Goodman and co-workers.¹⁸

It is obvious in Figure 1 that as more Pd (or Ni, Pd, Pt, or Rh) is added to the previously deposited monolayer, more CO is adsorbed. This recovery in the adsorptive property is completed when the metal film thickness reaches a few monolayers and the absorption approaches the single-crystal value. Sellidj and Koel²² found that this increase in the amount of CO on the surface was correlated with an increase in the CO desorption temperature, an increase in the CO heat of adsorption, and a shift in the C-O stretch mode in EELS, all suggestive of a weakening of the C-O bond and/or a strengthening of the CO-metal bond. At the time of our initial work on hydrogen uptake on Pd/Nb(110) and CO adsorption on Pd/Ta(110) monolayers, we advanced the view that *the modification of electronic structure of the Pd monolayer was responsible for the above mentioned trends in the hydrogen uptake or CO adsorption*. The low uptake of hydrogen on Pd monolayers was attributed to a lack of hydrogen dissociation and was attributed to the movement of the Pd 4d states below the Fermi level. For the case of CO adsorption, a similar conclusion was reached by recognizing the similarities between CO adsorption on 1 ML of Pd/Ta(110) and CO adsorption on Cu(111),⁴³ whose electronic structure resembles that of the monolayer, and CO adsorption on Pd(111),⁴⁴ whose electronic structure resembles that of the thickest Pd overlayers on Ta(110). Specifically, CO is less tightly bound on Cu(111) than Pd(111).

Surface Electronic Structure Changes in Metal Overlayers

Photoelectron spectroscopy⁴⁵ and inverse photoelectron spectroscopy⁴⁶ provide information about the valence electronic structure of surfaces and in our case characterize the differences in surface electronic structure between Pd(111) and Pd monolayers on Ta(110) or Nb(110). In particular, these techniques give information about the evolution of the electronic structure of the overlayer *and* its support as the metal coverage increases from that sufficient to form small isolated two-dimensional islands to that sufficient to form multilayers. The valence band photoelectron data in Figure 2 shows the changes in electronic structure of Pd/Ta(110) with increasing Pd coverage. The first curve shows the valence states for a clean Ta(110) surface where the Ta 5d states form a peak

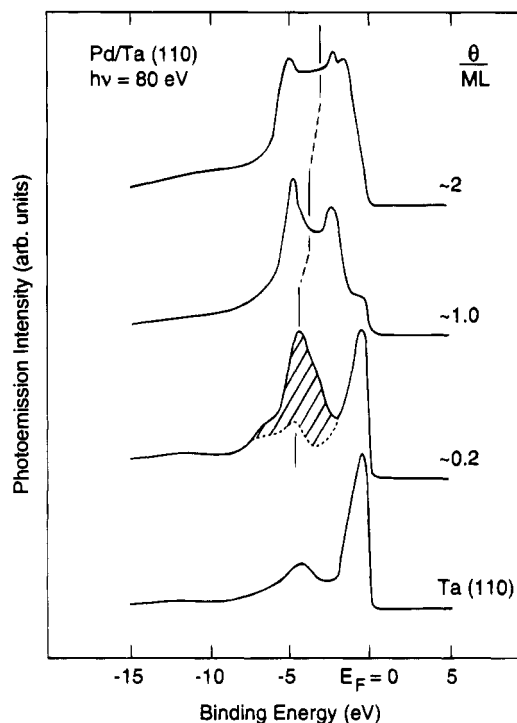


Figure 2. Photoelectron spectra detail the evolution of the electronic structure for clean Pd overlayers on Ta(110). The bottom curve shows the valence states of Ta(110). When a small ($\theta \sim 0.2$ ML) amount of Pd is deposited, Pd 4d states are added to the valence band (hatched area in the second curve). The thickest ($\theta \sim 2$ ML) Pd film has valence 4d states that resemble a Pd single crystal. The figure shows that the Pd 4d states evolve with increasing film thickness and that the monolayer has a small Pd 4d density of states at E_f . This is important for explaining the drastic changes in CO bonding to the Pd layer.

extending from E_f to about -2 eV binding energy. It is a convention to plot the binding energy as a negative value, and this signifies that electrons in such states are bound to the solid. After the deposition of a small ($\theta = 0.2$ ML) amount of Pd, the Pd 4d states (highlighted by the hatched shading) are found from 2 to 7 eV below the Fermi level (E_f) and the center of gravity of the Pd 4d states (marked by the vertical line above the second curve) at -4.5 eV is farther below E_f than for Pd(111)-like multilayers ($\theta \sim 2$ ML Pd coverage). This suggests that as the Pd coverage increases, the electronic states evolve toward those of a Pd(111) crystal surface. The curve for clean Ta(110) (dashed line) is superimposed over the second curve and shows that photoelectron emission from the Ta 5d states is attenuated as electrons go through the Pd overlayer. The amount of attenuation is greater when θ is increased to a monolayer. When sufficient Pd is added to form a monolayer, the Pd 4d states evolve and a second band between -2 and -3 eV is observed (third curve, Figure 2). The great reduction in photoelectron Pd 4d emission near E_f is easily seen in the third curve in Figure 2 and is larger than it appears in the spectrum because much of the photoelectron signal comes from the Ta support and not the Pd overlayer. The topmost curve shows Pd 4d states that look like a lot like those of a Pd crystal surface. For such a surface, the Fermi level cuts through the 4d band, and Pd has a large number of d states at the Fermi edge.⁴⁷ This is not the case for the Pd monolayer, for which the apparent shift of the d-band centroid away from

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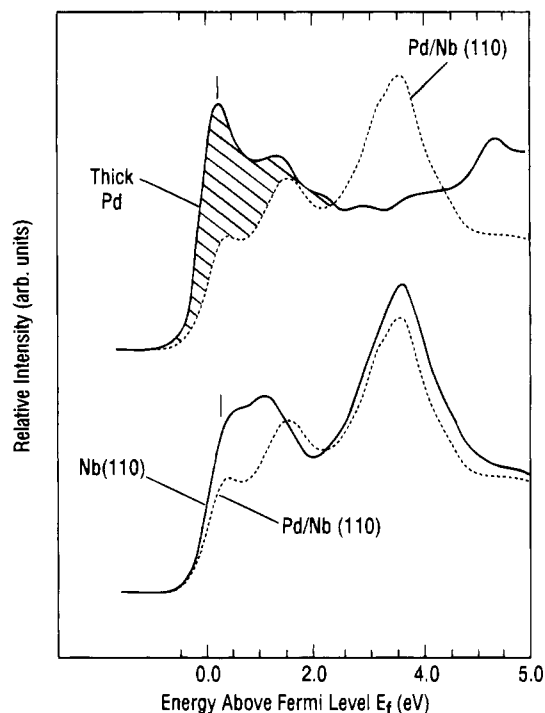


Figure 3. Inverse photoemission spectra for (1) Nb(110), (2) an epitaxial Pd(110) monolayer grown on Nb(110), and (3) a thick layer of Pd on clean Nb(110). Inverse photoemission which probes the unoccupied valence states shows the removal of unoccupied Pd 4d states and modifications of the Nb 4d states (i.e., a shift to higher energy) that could be explained by the formation of a bonding–antibonding couple with the Pd 4d states. Reprinted with permission from ref 50. Copyright 1988 American Institute of Physics.

the Fermi level is also accompanied by a narrowing of the 4d band and a sharp reduction in the 4d density of states near the Fermi edge. This trend in the d-band density of states (i.e., in going from bulk-like Pd(111) to 1 ML Pd/Ta(110)) is also seen for transition metals in going from group VIII to group IB (e.g., from Ni to Cu or from Pd to Ag).⁴⁸

As previously noted, we believe that a *chemical "interaction" between Pd and Ta is responsible for the modification of the Pd 4d states localized largely on the Pd overlayer.* Knowledge of the nature of this modification is crucial for understanding the subsequent chemical interactions between the Pd overlayer and adsorbates like CO or H₂. The interaction between Pd and Nb or Ta should change the electronic structure of the substrate near the interface between the overlayer and the substrate. For Pd/Nb(110) or Pd/Ta(110), inverse photoemission which probes the unoccupied electronic states is particularly useful in probing the electronic structure of the substrate. In the case of a Pd overlayer on Nb(110) or Ta(110), most of the Pd states are occupied, while the majority of the Nb 4d states are unoccupied.⁴⁹ Hence, inverse photoemission primarily probes the states which are localized on the Nb atoms. Momentum-resolved inverse photoemission (KRIPES) data for clean Nb(110) (bottom solid curve) and a Pd monolayer on Nb(110) (bottom dashed curve)^{20,50} are shown in Figure 3. When 1 ML of Pd is deposited on Nb(110), the KRIPES

intensity, which is proportional to the unoccupied Nb 4d dominated electron density of states, is reduced near the Fermi edge, when compared to Nb(110). In addition, the Nb 4d states near E_f (marked with a vertical line) seem to be shifted away from the Fermi level^{20,40} like the Pd 4d states probed by photoemission. The topmost solid curve shows a KRIPES spectrum for Pd(111), and the dashed line denotes Pd/Nb(110). Pd has a tail of unoccupied 4d states which cross the Fermi level and produce a peak (also marked with a vertical line) seen near the Fermi level. The KRIPES intensity, attributed to the Pd 4d states, is reduced (the hatched area) by the interaction between the Pd and Nb states which moves those Pd 4d states below E_f .

The electronic structure of layered bimetallic systems has been computed for a number of systems. For Pd/Nb(110) and Pd/Ta(110), tight binding methods have been used by Kumar and Benneman⁴⁹ and by Pick and Mikusik,⁵¹ respectively. El-Batannouny et al.¹⁰ used the linear-augmented plane wave (LAPW) method to do the first band structure calculations of Pd/Nb(110). In the most sophisticated attempt to compute the electronic structure, Weinert et al.²¹ used the full potential linear-augmented plane wave (FLAPW) method to determine the contributions to the valence states from the Pd and Nb in a Pd/Nb(110) bimetallic slab at each atomic site. The interaction between Pd and Nb drives the states, identified with the Pd site, farther below the Fermi level and causes a sharp drop in the partial density of states at E_f assigned to the palladium. For the Nb states the d band undergoes changes in the unoccupied states like those measured by KRIPES.

The computations, discussed in the preceding paragraph, describe the spectroscopic data very well. However, an idea taken from transition metal surface chemistry provides a better intuitive basis for understanding what is going on when metal atoms are deposited and interact with metal substrates. Surface chemistry is often explained by assuming that the adsorbate and the adjacent surface atoms can be treated as a cluster or *surface molecule*. The surface molecule concept⁵² states that the chemisorbed molecular states hybridize with the substrate d states to form bonding and antibonding levels that are broadened into surface resonances by interactions with the free electron-like s and p states. The concept of surface molecule can, obviously, be carried over to the adsorption of metal atoms on the same surfaces⁵³ and leads to the assignment of certain valence band features to bonding, nonbonding, or antibonding states. For the specific case of transition metals, the modification of the d states above and below E_f can be explained by "covalent" d-state bonding and the formation of bonding and antibonding levels from the hybridized d states. Our photoemission and inverse photoemission data for Pd/Ta(110) and Pd/Nb(110) show changes in binding energy of Pd 4d and Nb 4d states that can readily be attributed to the formation of a bonding–antibonding couple in which niobium and palladium contribute to the bonding states and Nb to the unoccupied antibonding states. This inter-

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action between the two metals implies that *significant changes occur in the distribution of charge around both metals but does not require significant transfer of charge from one metal to the other*. Although this is an oversimplification, it provides a natural explanation of the changing properties of supported metal monolayers. For example, the formation of d-d bonds between Ta and Pd shifts d charge away from both atom cores into the interstitial spaces between the atoms and, as experiment shows, shifts both the Ta 4f and Pd 3d core levels to deeper (larger) binding energies.⁵⁴

However, this is not the only interpretation of bimetallic layer behavior. Rodriguez and Goodman^{7,8} have advanced the view that significant amounts of charge are transferred from the palladium monolayer to the substrate and that this accounts for the reduced CO-metal interaction. Their experimental evidence, derived from a direct reading of photoelectron data, is that (1) a reduction in the metal core level binding energy like that observed when metals are oxidized occurs and (2) a reduction in the work function like that observed when surface charge is reduced takes place. On a superficial level, this suggestion conflicts with the fact that palladium is more electronegative than tantalum. The suggestion also is in conflict with calculations^{10,21,49,51} that indicate that the amount of charge transfer from the Nb to the Pd is too small to account for core level shifts.

Direct readings of photoelectron data can be misleading. The interpretation of core level shift data and its meaning has long been a subject of controversy among scientists studying metallic compounds, alloys, thin films, and clusters on various substrates.⁵⁵⁻⁵⁷ Many investigators apply the principle developed by Siegbahn and co-workers⁵⁸ for the chemical analysis of molecular species, which is based on the idea that the core level binding energy is related to the effective atomic charge. This leads to the simple and apparently intuitive view that as charge is removed from an atomic site, the core level shifts to higher binding energy. Implicit in this analysis are the assumptions that (1) the reference energy levels stay more or less fixed and (2) final state effects are the same for dissimilar systems, even though this latter effect approaches 10 eV in calculations.

Core level shifts have been studied in bulk alloys, and an excellent summary of results for a number of bimetallic systems can be found in a paper by Steiner and Hüfner.⁵⁹ Many of the bimetallics studied by Steiner and Hüfner are similar to the Pd/Nb(110) or Pd/Ta(110) systems discussed in the preceding sections. What is important in such data is that a wide variety of behavior occurs and either the core levels can shift in opposite directions or both core levels can shift in the same direction. Two examples of the latter behavior are the Pd/Zr and Pd/Ti couples where the

core levels of both alloy components shift in the same direction to higher binding energy. On the basis of electronegativity arguments, it would be predicted that charge would be removed from Pd, the cation, and transferred to the Ti or Zr anion.⁶⁰ Hence, the charge removed from one site must add to the charge on the other site and it would be expected that the core levels would move in opposite directions. Obviously, this does not happen, and additional phenomena must be invoked to explain the core level shifts.^{55,61} These phenomena include (1) intraatomic charge transfer (e.g., d to sp interchange); (2) final state effects; (3) extraatomic (Madelung) potential terms; (4) covalent bonding contributions over and above their contributions to site electron count changes, including volume effects due to deviations from Vegard's law; and (5) charge tailing, i.e., the effective medium due to an atom's neighbors that affects electron site counts.

In various alloy systems, the importance of the above factors can vary, and there are detailed discussions in the literature. Ta 4f core level data for the Pd/Ta(110) system has already been published,¹³ and data for the Pd 3d levels was recently measured for comparison with the data of Rodriguez and Goodman.⁷ Figures 4 and 5 show the data for Pd monolayers on Ta(110), and it can be seen that the Pd 3d core levels and the surface-related Ta 4f core level components shift -1.2 or -0.3 eV to greater binding energy, respectively. The core level binding energy shifts of Pd/Ta(110) resemble those of the Pd/Zr and Pd/Ti couples already mentioned. Besides the monolayer system itself, thin films of Pd/Ta compounds can be made by heating thicker Pd overlayers and mixing the Pd with the Ta, and this also causes *both* core levels to shift to the *same* higher binding energy. At this point there are three important things to emphasize. First, there is no qualitative difference between the result for the monolayer and the alloyed region at the surface. Second, both core levels shift in the same direction with alloying or surface bonding, and we emphasize that this is not unusual in alloy systems. Third, the shifts of the Ta 4f and Pd 3d core levels cannot be understood by a simple charge-transfer picture. If anything, the data argues for the removal of charge from *both* sites and its localization between the Pd and Ta atoms, as would be expected from the formation of a bonding-antibonding couple.

A final point to be discussed is the variation in the photoelectron work function shown in Figure 6. It has been suggested that the reduction in the work function (ϕ) when Pd or a similar metal is deposited on an early transition metal is related to charge transfer between the overlayer and substrate. This decrease in work function is seen in the data plotted in Figure 6 for group VIII and IB metal overlayers on Nb(110). In most cases, the work function decreases for coverages less than a monolayer. The work function depends on the Fermi level position and the magnitude of the surface dipole created by charge that projects into the vacuum. States that are more delocalized (e.g., s and p states) make a bigger contribution to the work function magnitude than states that are more localized

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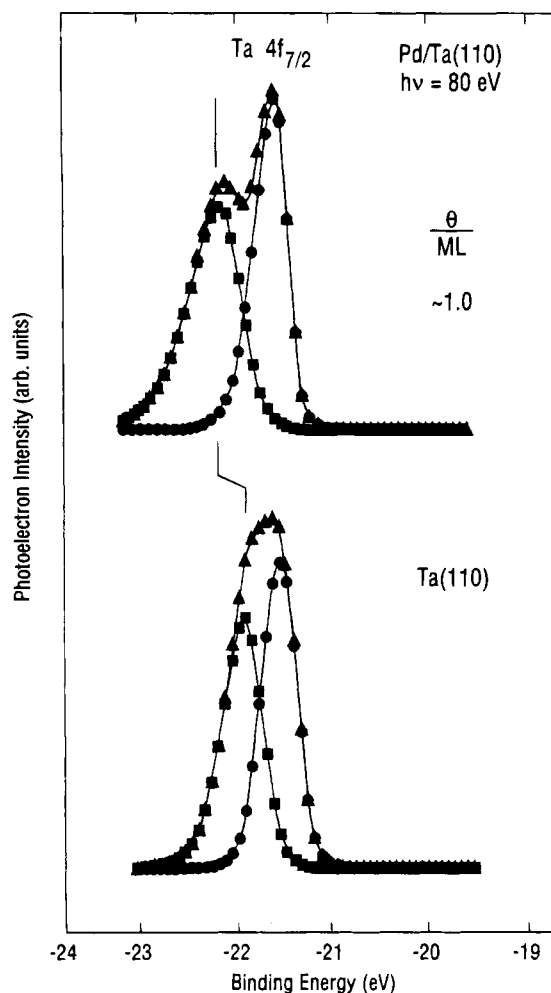


Figure 4. Expanded view of the Ta $4f_{7/2}$ core level after background subtraction and a fitting of peaks to provide a hypothetical decomposition of the core level into bulk and surface components (related to the topmost layer of atoms). For clean Ta(110), we find the bulk peak at -21.5 eV and the surface peak at -21.9 ((110) face). When the surface is covered by a monolayer of Pd, the surface peak shifts -0.3 eV to greater binding energy while the binding energy of the bulk peak remains unchanged. The shift of the Ta $4f$ surface components is due to the bonding of the surface atoms to Pd at what is now an interface between the overlayer and substrate.

to atom sites (e.g., d states).⁶² However, the more localized states play the bigger role in determining the sign and magnitude of the core level shifts. Hence, any correlation between core level shifts and work function in transition metals is not obvious. An example of the fortuitous nature of work function–core level shift correlation can be seen in the case of Pt and Pd on Ta(110). Both systems have core level components which move to deeper binding energy when the monolayer is deposited on the substrate. However, the work function increases during the growth of the Pt monolayer and decreases during the growth of the Pd monolayer. Hence, there is no simple correlation.

Effect of Overlayer Electronic Structure on Chemisorption

We assert that the dramatic changes in CO adsorption on early transition metal supported Pd overlayers

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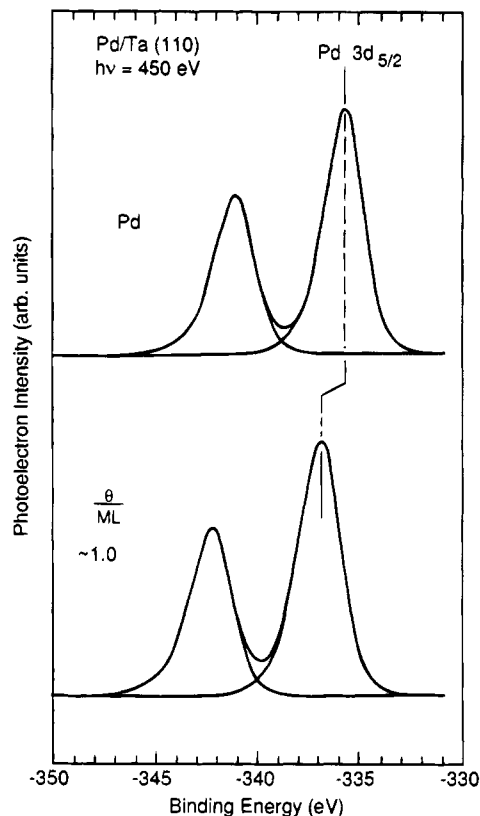


Figure 5. The above figure shows the Pd $3d$ core levels and a fit with Voigt functions to pinpoint the locations of the peaks. The bottom curve is for a monolayer of Pd on Ta(110) and the top curve for multilayer Pd coverage on the same surface. The binding energy of the Pd $3d$ core level decreases as the Pd thickness is increased from a monolayer to several layers thickness. The Pd $3d$ core level shifts ~ 1.2 eV to lower binding energy. The bonding between Pd and Ta causes the Pd $3d$ core levels to shift -1.2 eV to greater binding energy for the monolayer as compared to Pd metal.

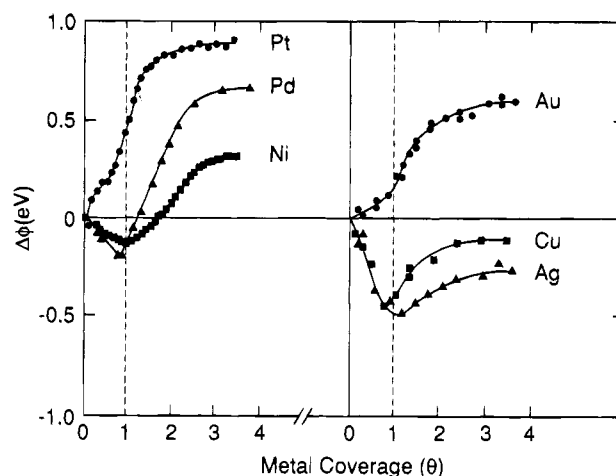


Figure 6. Photoelectron-derived measurements of the work function change ($\Delta\phi$) as a function of metal coverage for transition metal and noble metal films on Nb(110). The data shows that in most cases the work function decreases when an atomically thin overlayer is grown. However, this is not the case for Au or Pt where the work function increases.

are primarily due to the modification of the Pd $4d$ states from a noble metal-like electronic structure to the palladium metal electronic structure as the overlayer thickness increases. In the regime below one monolayer Pd coverage, the decrease in dissociative chemisorption of CO can be explained by the fact that the Pd islands covering the tantalum surface are like

the completed monolayer, in that they are unable to form sufficiently strong CO-metal bonds for the retention of CO at 300 K. The islands block an increasing fraction of the tantalum surface as more palladium is deposited on the surface. At one Pd monolayer coverage, the tantalum surface is completely covered by a commensurate layer of Pd in the Ta(110) structure, and this surface adsorbs the little or no CO. For many of the bimetallic systems studied, it was found that dissociated and chemisorbed CO coexist on the surfaces over a neighborhood around the metal coverage needed to assemble a complete monolayer. We found that such systems either depart from 2-D thin film growth¹⁶⁻¹⁸ or in the case of Rh/Mo(110) have a significant number of d states or conversely d-state holes at the Fermi edge.¹⁹

With the addition of Pd to the completed monolayer the structure of the Pd layer transforms to the Pd-(111) structure and the number of d states (and presumably s and p states) starts to approach that of bulk Pd(111) surface. The surface-based studies of the strength of the CO-metal bond show a systematic increase with the increase in the valence density of states at E_f . It should be emphasized that this phenomenon is common to all of the metal films studied. It should also be noted that certain features of the CO-metal interaction⁶³ (i.e., the dative metal-5 σ bond) are not shared by other simple molecules like O₂ or H₂,^{64,65} and the reduction in the sticking coefficient may not occur for molecular adsorbates in general. However, another example of the greatly changed chemistry of the monolayer system was also found for the case of hydrogen absorption through the Pd into the bulk Nb or Ta.^{12,66-68} In this case, the smallest amount of uptake into the bulk occurred for the monolayer, and it is only with increasing amounts of Pd that the uptake of hydrogen increases by several orders of magnitude. It is thought that hydrogen molecules do not dissociate on the monolayer surface, and hence the uptake into the bulk is greatly reduced.¹² The key point to be drawn from the work just described is that a specific chemical property is related to an identifiable modification of the surface valence electronic structure.

The application of the surface molecule concept⁵² previously used to explain the change in the electronic structure of the metal overlayer again provides an intuitive basis for understanding the diverse physical and chemical phenomena of metal-metal systems like Pd/Nb(110). The modification of the monolayer electronic structure due to the bonding of the Pd or similar metal with Nb or similar metal serves to decrease the bonding between adsorbates like CO and the metal. Our understanding of the bonding of CO with metals is based on the seminal work of Blyholder.⁶⁹ Blyholder proposed that the CO 5 σ state hybridizes with the metal d or p states and forms resonances in the valence bands and electrons are transferred from CO to the metal. This is counterbalanced by backdonation of charge from the metal into the CO 2 π^* level. Sung

and Hoffman⁷⁰ have noted that the CO 2 π^* and the metal states near the Fermi edge can be considered "frontier orbitals" in the sense in which this concept is used to understand molecular bonding. In such a case, the CO 2 π^* and the metal d states hybridize to form resonances with metal character below E_f and with 2 π^* character above.⁷¹ The bonding of CO to Pd is reduced on our Pd surfaces because the density of states at E_f is reduced and the Pd d states are shifted away from E_f . They lack (1) the d-state holes needed to hybridize the metal d states with the CO 5 σ level to form the dative bond or (2) the filled states at the Fermi level (acting like the HOMO frontier orbital) needed for bond formation with the CO 2 π^* level. The modification of the chemical properties of Pd and similar metal monolayers is large because the reduction in the number of occupied and unoccupied metal d states seen by the adsorbate is large. We believe that the number of occupied and unoccupied states at the Fermi surface controls the bonding of adsorbates in the cases examined.

Summary and Conclusions

This Account has discussed the chemical behavior of early transition metal surfaces covered by late transition metal overlayers. It shows that the chemical behavior of the composite surface changes in a systematic way with overlayer coverage and indicates that the chemical changes occur in tandem with changes in the physical properties of the surface, namely, the electronic structure. We interpret the electronic structure changes using well-known chemical and physical concepts as they are applied to surfaces and thin films. Specifically, we find that the bonding between metal overlayer and metal substrate causes the changes in the overlayer electronic structure. More specifically, the bonding reduces the number of occupied and unoccupied states near the Fermi level. Although this interaction leads to charge redistribution through the hybridization of the states from each atom, it does not follow that large amounts of charge shift from one element to the other. We assert that a specific change in the overlayer valence electronic structure, namely, the change in the number of occupied and unoccupied states near the Fermi level, plays a crucial role in the bonding of CO to the surface and the dissociation of molecular hydrogen on the surface because those metal states are involved in bond formation with the adsorbates.

The authors thank J. W. Davenport, M. Weinert, and R. E. Watson for their valuable comments and criticisms and also acknowledge the contributions of Xiaohu Pan and Liqiang Jiang to the research discussed in this Account. We especially thank Peter D. Johnson for allowing us to reproduce data from his previous work published in Physical Review B. We gratefully acknowledge financial support from the U.S. Department of Energy, Division of Materials Sciences (Contract No. DE-AC02-76CH00016).

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