PHYSICAL REVIEW B VOLUME 46, NUMBER 11 15 SEPTEMBER 1992-I

Chemical and electronic properties of ultrathin metal films: The Pd/Re(0001) and Pd/Ru(0001) systems

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(Received 28 February 1992)

The nature of the electronic and chemical properties of ultrathin Pd films on Re(0001) and Ru(0001) has been studied using x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and CO chemisorption. The results indicate that the Pd($3d_{5/2}$) binding energy for a monolayer (ML) of Pd on Re(0001) and Ru(0001) is perturbed by +0.60 and +0.30 eV, respectively, from that of the surface atoms of Pd(100). These electronic perturbations induce large changes in the chemical properties of the Pd films. TPD results indicate that the desorption temperature of CO from 1 ML of Pd on Re(0001) and Ru(0001) is ~120 K lower than the corresponding desorption temperature from Pd(100). The XPS and CO-TPD data indicate that Pd transfers charge to the Re and Ru substrates, becoming electron deficient and less efficient at π backdonation toward CO. By comparison of these results with those reported previously for Pd, Ni, and Cu adlayers, a correlation is observed among the electronic perturbations of the adlayers, the cohesive metal-substrate bond strength, the ability of the film to chemisorb CO, and the CO-induced shift in the metal core-level binding energy. In general, the results indicate that the formation of a metal-metal bond at a surface leads to a gain of electron density by the element initially having the greater fraction of empty states in its valence band. This behavior is completely contrary to that seen in bulk alloys, likely a consequence of the anisotropic character of a surface that changes the relative electronegativities of the metal atoms. On the basis of these results, a qualitative scale of surface electronegativities is developed, showing trends that are very different from those found in three-dimensional bulk alloys.

I. INTRODUCTION

Studies of the electronic and chemical properties of ultrathin Pd films supported on single-crystal metal surfaces have received considerable attention over the past several years,[1,2] and are a first step in delineating the fundamental properties of industrial bimetallic catalysts containing Pd.[3] These studies have shown that the properties of a supported Pd monolayer can be perturbed greatly with respect to those of bulk Pd. X-ray photoelectron spectroscopy (XPS) results show that Pd atoms in a monolayer of Pd on W(110),[4] $Pd_{1.0}$/W(110), or on Mo(110),[5] $Pd_{1.0}$/Mo(110), have a higher Pd($3d_{5/2}$) binding energy than both the bulk and surface atoms of Pd(100). For example, in the case of $Pd_{1.0}$/W(110) the Pd($3d_{5/2}$) peak position is 0.80 eV higher in energy than that of the surface layer of Pd(100).[4] This is consistent with transfer of charge from the Pd overlayers to the substrate. Similar trends have been observed using valence-level photoemission spectroscopy (UPS) for monolayer Pd films on Ta(110),[6] Nb(110),[7] and W(110).[8] Since the electronic properties of these monolayer systems are altered, it is not surprising that the chemical properties also change. This is apparent in the temperature programmed desorption (TPD) results of CO from a monolayer of Pd on Ta(110),[9] where the desorption temperature is ~235 K lower than that from Pd(100).[10] A similar reduction in the CO-desorption temperature has been observed for CO on $Pd_{1.0}$/W(110) and $Pd_{1.0}$/W(100).[11] The photoemission and CO-TPD data indicate that Pd transfers charge to the Ta and W substrates, becoming electron deficient and less efficient at π backdonation to CO.[4,5]

As part of an effort to understand the structural and electronic properties responsible for the enhanced catalytic properties of bimetallic systems involving Pd, our laboratory has initiated a systematic study of the properties of Pd films supported on several transition-metal substrates. In this paper we report the results for the Pd/Re(0001) and Pd/Ru(0001) systems, and compare them with data for the deposition of Pd onto early transition metals.[4-9,11-13] XPS and TPD have been used to examine the nature of the physical and electronic interactions of Pd adlayers with the Re(0001) and Ru(0001) substrates. The chemisorption of CO onto these Pd overlayer surfaces has been studied, as well as H_2 adsorption onto the Pd/Re(0001) surface.

In comparing the present results with those for other Pd, Ni, and Cu monolayer systems, general trends are apparent regarding the chemistry and electronic properties of bimetallic systems. For example, these results yield information about metal-substrate bond strengths, and the chemisorptive properties of these systems. Furthermore, these studies indicate that charge transfer plays an important role in the bonding of an overlayer metal to the substrate. A theory is described which develops the conceptual framework to qualitatively predict electronic changes in the bonding of two different metals at a surface. The trends observed in XPS and CO TPD provide convincing evidence that the electronegativity of surface atoms is quite different from that found for bulk atoms.

By using carbon monoxide as a probe molecule, an excellent correlation is demonstrated between the electronic character of a metal overlayer and its chemical properties.

II. EXPERIMENT

A conventional ultrahigh-vacuum chamber with a base pressure of $\leq 4\times10^{-10}$ Torr was used for this work. The system was equipped with Auger electron spectroscopy (AES), XPS, low-energy electron diffraction (LEED), and TPD capabilities.[14]

The sample manipulator allowed for resistive heating to 1600 K and liquid-nitrogen cooling to 115 K. An electron beam assembly was used for flashing the sample to 2300 K. The Re(0001) and Ru(0001) crystals were mounted by spotwelding to Ta support leads and the surface temperature was monitored by a W/5%Re-W/26%Re thermocouple spotwelded to the sample edge. The surfaces were cleaned by successive cycles of oxidation and annealing as reported in the literature.[15] The cleanliness and long-range order were verified with AES, XPS, and LEED.

Pd was evaporated onto the crystal surface at a substrate temperature of ~350 K (unless stated otherwise) by resistively heating a Ta wire wrapped with high purity Pd wire. Following evaporation the surfaces were heated to 500 K, and subsequently verified to be clean by AES or XPS. All adsorbate coverages are reported with respect to the number of surface atoms [Re(0001), 1.52×10^{15} atoms/cm^2; Ru(0001), 1.57×10^{15} atoms/cm^2], with one Pd atom per substrate atom corresponding to $\Theta_{\mathrm{Pd}}=1.0$.

A linear heating rate of 10 K/s was used in all the desorption experiments.

The Pd(3*d*), Ru(3*d*), and Re(4*f*) XPS spectra in Sec. III were obtained with an Al $K\alpha$ x-ray source. The Pd($3d_{5/2}$) binding energies were referenced against the Re($4f_{7/2}$) or the Ru($3d_{5/2}$) peak and have an experimental error of ±0.03 eV. Detection was normal to the surface in XPS and AES.

III. RESULTS

A. Pd films on Re(0001)

The desorption spectra of Pd from the Re(0001) surface are shown in Fig. 1. Two desorption states of Pd are apparent, typical of Pd desorption from single-crystal transition-metal substrates.[11] The high-temperature state (1350–1500 K) is attributed to desorption of the first Pd monolayer. The low-temperature state (1100–1350 K) is due to multilayer Pd desorption and displays a common leading edge, characteristic of zero-order thermal desorption. Using the saturation of the high-temperature state as $\Theta_{\mathrm{Pd}}=1.0$ monolayer (ML), TPD area analysis was used to calculate all Pd coverages in this section. A (1×1) LEED pattern was observed for all submonolayer Pd coverages.

In Fig. 2, the binding energy of the Pd($3d_{5/2}$) XPS level is plotted as a function of Pd coverage in monolayers. Representative spectra of the Pd(3*d*) XPS region, from which part of the data in Fig. 2 were obtained, can be seen in Fig. 3. The spectra were acquired after depositing the Pd onto the Re(0001) substrate at ~350 K with a subsequent anneal to 500 K. At submonolayer coverages the binding energy of the Pd($3d_{5/2}$) peak shifts from 336.15 eV for the 0.20-ML coverage to 336.00 eV at 1 ML. Increasing the Pd coverage further results in a binding energy decrease to 335.65 eV at ~7 ML. Beyond a Pd coverage of ~7 ML there is no change in the Pd($3d_{5/2}$) peak position. For $\Theta_{\mathrm{Pd}}\leq 1$ ML, the binding energy measured for Pd is larger than that of bulk Pd. This trend is totally contrary to that seen on Pd(100),[16,17] where the surface atoms appear at ~0.4 eV toward *lower* binding energy than the bulk atoms. This difference is consistent with a bonding model in which electron density is transferred from Pd to Re. A similar model has been proposed to explain changes in work function and Pd($3d_{5/2}$) binding energy for Pd$_{1.0}$/W(110),[4] i.e., $\mathrm{Pd}^{\delta+}-\mathrm{W}^{\delta-}$.

CO and H_2 chemisorption were used to investigate

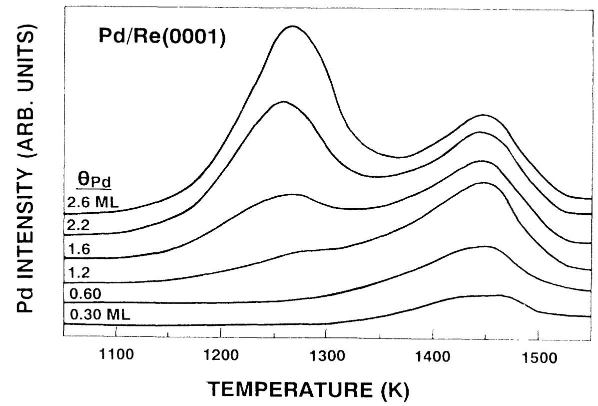

FIG. 1. Thermal desorption spectra ($m/e=106$) for Pd films on Re(0001). Pd was vapor deposited at a sample temperature of ~350 K, and the surface was annealed to 500 K before acquiring the spectra.

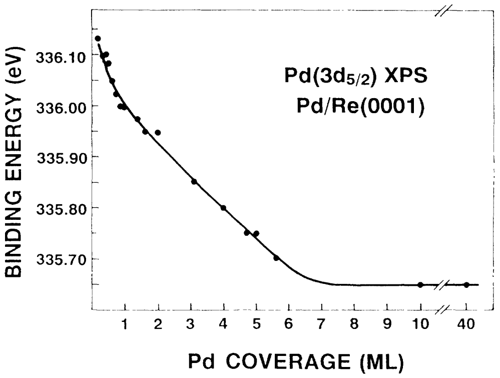

FIG. 2. Pd($3d_{5/2}$) XPS binding energy for Pd on Re(0001) as a function of Pd coverage. The Pd films were deposited at ~350 K and annealed to 500 K before taking the spectra.

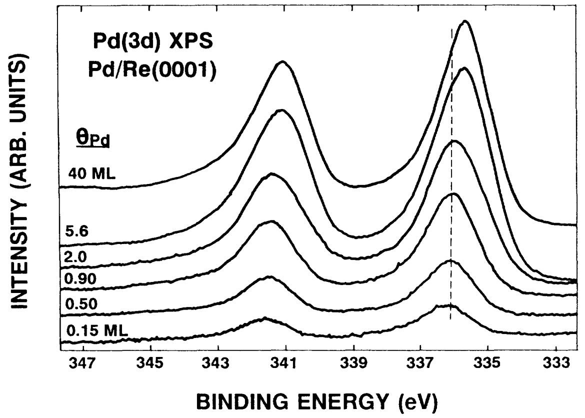

FIG. 3. Pd(3*d*) XPS spectra for the Pd/Re(0001) system as a function of Pd coverage.

changes in the chemical properties of the supported palladium films. TPD spectra are shown in Fig. 4 for CO desorption as a function of Pd coverage on Re(0001). The spectra were taken after a 10-L (1 L$=10^{-6}$ Torr s) exposure of CO (sufficient to reach saturation) to Pd/Re(0001) surfaces at 115 K. The CO desorption spectrum from Re(0001) contains three states between 250 and 600 K, which are attributed to desorption of molecularly adsorbed CO, and a fourth state between 700 and 900 K assigned to the recombination of dissociated CO. These results are in agreement with previous work.[18] For increasing Pd coverages up to 1 ML, the contribution from the low-temperature CO-desorption states from Re(0001) are gradually attenuated while a new peak appears at 360 K. This new feature is attributed to desorption of molecularly adsorbed CO on Pd. Also, for increasing submonolayer Pd coverages, the high-temperature CO recombination state from Re(0001) moved to a lower temperature and decreased in intensity (not shown). Pd coverages of greater than 1 ML showed no observable CO recombination peak. In Fig. 4, an increase in the Pd coverage beyond 1 ML results in the attenuation of the 360-K peak while a feature at 430 K grows in intensity. This 430-K feature shifts to higher temperature as the Pd coverage increases, reaching a value of ~470 K at $\Theta_{\mathrm{Pd}}=3$ ML. This desorption temperature is very close to those temperatures reported for CO on Pd(100) (Ref. 10) and Pd(111),[19] indicating that the Pd-Re interaction is relatively short range in nature. In Fig. 2, variations in the core-level binding energy are observed up to a Pd coverage of ~6 ML, likely because the photoemission results are a superposition of several metal atom layers and include contributions from the Pd-Re interface.

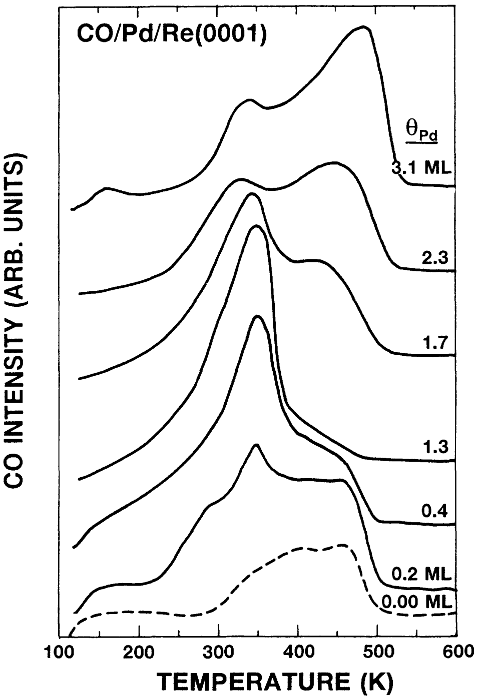

FIG. 4. Thermal desorption spectra of CO ($m/e=28$) from Pd-covered Re(0001) surfaces. The Pd films were prepared by depositing the Pd at a substrate temperature of ~350 K, followed by annealing to 500 K. The spectra were then taken after cooling the surface to ~115 K and dosing with 10 L of CO. The clean Re(0001) TPD spectrum is not normalized for area.

The TPD results indicate that the desorption temperature of CO from $\mathrm{Pd}_{1.0}$/Re(0001) is ~110 K lower than that from Pd(100), that is, the Pd-Re interaction significantly weakens the strength of the Pd-CO bond. Photoemission studies also show a decrease in the interaction between Pd and CO when the metal is supported on Re(0001). The Pd(3*d*) XPS spectra for clean and CO-saturated Pd films, $\Theta_{\mathrm{Pd}}=0.25$ and 1 ML, are shown in Fig. 5. The Pd surfaces were prepared by depositing Pd at ~350 K, annealing to 500 K, after which the clean spectra were acquired. The sample was then cooled to ~115 K, dosed with 10 L of CO, and the CO-saturated spectra obtained. The adsorption of CO induces a shift of +0.55 eV in the Pd($3d_{5/2}$) peak position from that of clean Pd. This CO-induced shift is much smaller than the shift of ~+1.2 eV seen for the surface atoms of

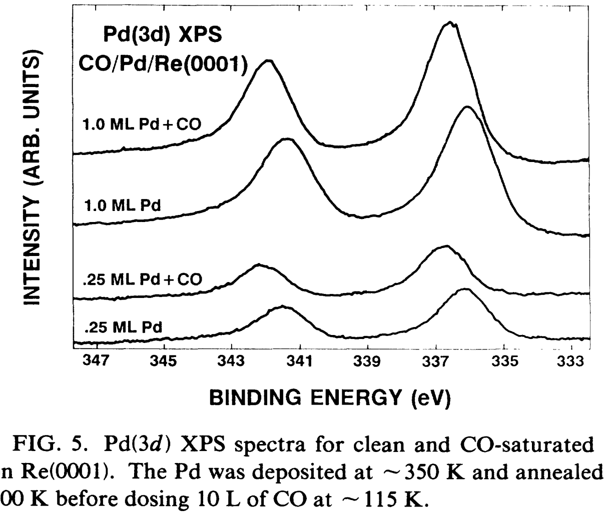

FIG. 5. Pd(3*d*) XPS spectra for clean and CO-saturated Pd on Re(0001). The Pd was deposited at ~350 K and annealed to 500 K before dosing 10 L of CO at ~115 K.

Pd(100) upon CO adsorption.[17,60] The effects of CO adsorption on the Pd($3d_{5/2}$) binding energy of Pd/Re(0001) were reversible. Upon desorption of the CO, the Pd($3d_{5/2}$) binding energy was found to be identical to that observed before adsorption of the molecule.

In Fig. 6 the effect of hydrogen adsorption on the Pd($3d$) XPS spectra is shown for three Pd coverages (Θ_{Pd}=0.25, 0.50, and 1.25 ML). The samples were prepared as for the CO/Pd/Re(0001) system with the substitution of H_2 for CO. A shift in the Pd($3d_{5/2}$) peak position is evident upon adsorption of hydrogen. The magnitude of the induced shift is found to change from 0.20 eV at the 0.25- and 0.50-ML Pd coverages to 0.30 eV at a coverage of 1.25 ML. As with CO adsorption the effects of H_2 adsorption are reversible; that is, the Pd($3d_{5/2}$) binding energy returns to the clean Pd value upon desorption of the hydrogen.

The results for the H/Pd/Re(0001) system are similar to those found for other studies of hydrogen adsorption on Pd(100) (Ref. 16) and mixed-metal systems containing Cu and Ni.[20,21] Consistent with these previous studies, the adsorption of hydrogen shifts the Pd($3d_{5/2}$) peak position to a higher binding energy. In contrast to the previous studies, the $\mathrm{Pd}_{1.25}$/Re(0001) system did not show a decrease in the magnitude of the adsorbate-induced shift for Pd coverages of greater than 1 ML. If hydrogen remains on the surface, a decrease in the magnitude of the adsorbate-induced shift is expected for admetal coverages of greater than 1 ML due to the increased contribution to the binding energy measurement of the subsurface atoms,[20,21] which are not affected by hydrogen bonding. It has been shown for Pd that hydrogen diffuses into the bulk of the metal.[22–25] The results for the $\mathrm{Pd}_{1.25}$/Re(0001) system are consistent with hydrogen diffusion into the subsurface region altering the chemical environment of the bulk Pd atoms and perturbing the Pd($3d_{5/2}$) binding energy.

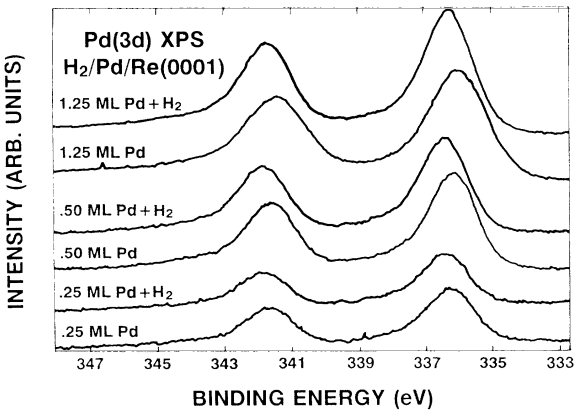

FIG. 6. Effects of hydrogen on the Pd($3d$) XPS spectra for Pd/Re(0001) systems. The surface was exposed to 10 L of hydrogen after the Pd was dosed at ~350 K with a subsequent anneal to 500 K.

B. Pd films on Ru(0001)

The interaction between Pd and "Ru(0001)" surfaces [generated by depositing thick Ru films onto a Mo(110) crystal] has been studied previously by AES, LEED, and CO chemisorption at room temperature by Park.[26] The results indicate that the first few Pd monolayers grow in a layer-by-layer mechanism with the first monolayer growing pseudomorphic with respect to the "Ru(0001)" substrate. For CO exposures at ~300 K, the amount of CO adsorbed onto the bimetallic surface decreased by ~80% when the Pd coverage was increased from 0 to 0.9 ML.[26] The CO-TPD results for 0.9 ML of Pd on "Ru(0001)" showed a small desorption peak centered at ~380 K. The fact that CO is not adsorbed extensively on the supported Pd at room temperature suggests that there is a significant interaction between Pd and the Ru substrate. We have investigated the extent of this interaction using TPD, XPS, and a Ru(0001) single-crystal substrate.

Figure 7 shows the TPD spectra for several Pd coverages on Ru(0001). The Pd desorption features for the Pd/Ru(0001) system are very similar to those observed for the Pd/Re(0001) system. A high-temperature state corresponding to desorption of the first monolayer is centered at temperatures between 1410 and 1440 K. The multilayer Pd desorption state is found in the temperature range 1150–1350 K. These peaks have a common leading edge and grow in intensity with increasing Pd coverage. TPD area analysis was used to calculate all Pd coverages in this section with the saturation of the high-temperature state being defined as 1.0 ML. Submonolayer Pd coverages indicated a (1×1) LEED pattern.

The Pd($3d$) XPS region for Pd coverages of 0.45, 1.2, 2.0, 2.9, and 15 ML on Ru(0001) is shown in Fig. 8. The Pd films were prepared by depositing the Pd at a sub-

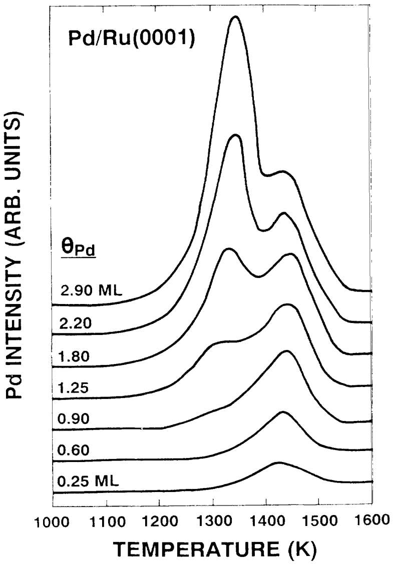

FIG. 7. The thermal desorption spectra of Pd ($m/e=106$) from the Ru(0001) substrate. The Pd was deposited at a substrate temperature of ~350 K and subsequently annealed to 500 K.

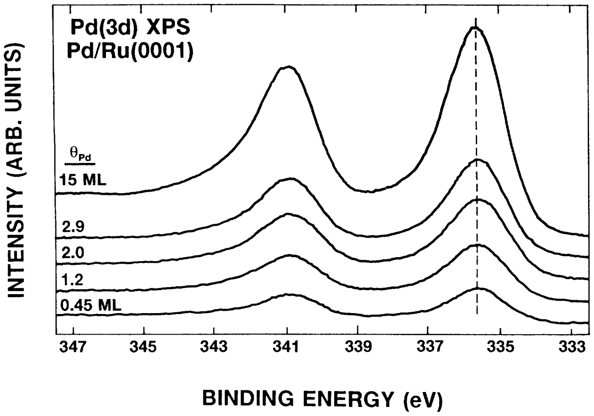

FIG. 8. Pd(3*d*) XPS spectra for Pd films on the Ru(0001) substrate. The Pd was deposited at ~350 K and annealed to 500 K, before acquiring the spectra.

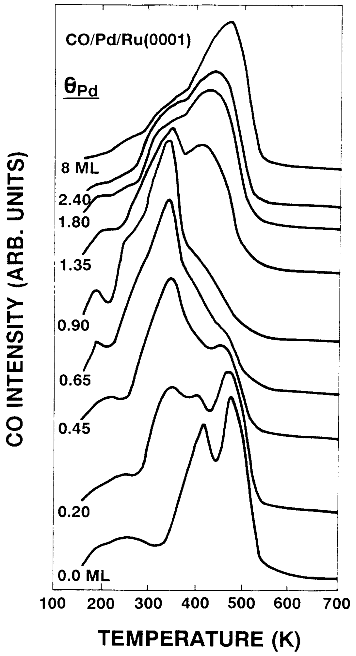

FIG. 9. CO thermal desorption spectra ($m/e=28$) from Ru(0001) and Pd/Ru(0001) systems. The spectra were taken after cooling the surface to 115 K and dosing with 10 L of CO. The Pd films were previously deposited at ~350 K and annealed to 500 K.

strate temperature of ~350 K, followed by a 500-K anneal. The Pd($3d_{5/2}$) peak remains constant for all Pd coverages at a binding energy of 335.65 eV. That is, the binding energy of 1 ML of Pd supported on Ru(0001) is very close to the binding energy found for the subsurface atoms of pure Pd. This behavior is very different from that of Pd(100), where the surface atoms have a *lower* binding energy (~ −0.4 eV) (Refs. 16 and 17) than the subsurface atoms, or in Pd on W(110) (Ref. 4) and Re(0001), where the supported monolayers of Pd appear at *higher* binding energies than the subsurface atoms of pure Pd. The XPS results indicate that the electronic perturbations are most significant when Pd bonds to early transition metals. This is consistent with measurements which show a larger decrease in the work function for $\mathrm{Pd}_{\leq 1.0}$/W(110) (Ref. 12) than for $\mathrm{Pd}_{\leq 1.0}$/"Ru(0001)."[26] Thus the transfer of electrons from Pd to the metal substrate appears to become more significant with an increase in the fraction of empty states in the valence band of the substrate.

TPD spectra for saturation coverages of CO from Pd/Ru(0001) are shown in Fig. 9 as a function of Pd coverage and compared with CO desorption from Ru(0001). The Pd films were deposited at a substrate temperature of ~350 K followed by an anneal to 500 K. The surface was then cooled to 115 K and dosed with a saturation coverage of CO (10 L) followed by the acquisition of the TPD spectra. At submonolayer coverages the two peaks that are attributed to CO desorption from the Ru(0001) surface at 400 and 475 K (Refs. 27 and 28) are attenuated with increasing Pd coverage. Concomitantly a new desorption feature appears at ~345 K, which is attributed to CO desorption from Pd atoms supported on Ru(0001). The apparent difference between our CO-TPD experiments and those reported previously for CO/Pd/"Ru(0001)" (Ref. 26) is likely a consequence of the difference in the CO-dosing temperature (115 K in this work versus ~300 K in Ref. 26).

In Fig. 9, Pd films greater than one monolayer show no features due to CO desorption from the Ru(0001) surface. Increasing the Pd coverage beyond one monolayer results in the 345-K peak decreasing in intensity, while a new shoulder appears at ~425 K. This peak is attributed to desorption of CO from three-dimensional islands of Pd and moves to higher temperatures with increasing Pd coverage, approaching the desorption temperature of CO from Pd(100) (~470 K).[13] A monolayer of Pd supported on Ru(0001) has a CO-desorption temperature 125 K lower than that from a pure Pd substrate. This reduction in desorption temperature corresponds to a weakening of ~8 kcal/mol in the strength of the Pd-CO bond.

The effects of CO chemisorption on the electronic properties of Pd overlayers were monitored using the induced shift in the Pd($3d_{5/2}$) binding energy. In Fig. 10 the Pd(3*d*) XPS region is shown for clean and CO-saturated Pd/Ru(0001) surfaces (with $\Theta_{\mathrm{Pd}}=0.3$ and 0.8 ML). The Pd was evaporated onto the Ru(0001) crystal at a substrate temperature of ~350 K, the surface flashed to 500 K, and the clean Pd(3*d*) spectra then acquired. Subsequently, the sample was cooled to ~115 K, dosed with a saturation exposure of CO (10 L), and the Pd(3*d*) XPS region then scanned. Adsorption of CO shifted the Pd($3d_{5/2}$) binding energy by +0.80 eV with respect to the peak position observed for the clean Pd/Ru surfaces. This shift is smaller than that induced by CO on the surface atoms of Pd(100) [~ +1.2 eV (Refs. 17 and 60)]. Thus the photoemission results are consistent with the CO-TPD data in Fig. 9, indicating that the Pd-Ru interaction weakens the Pd-CO bond. The induced shift on

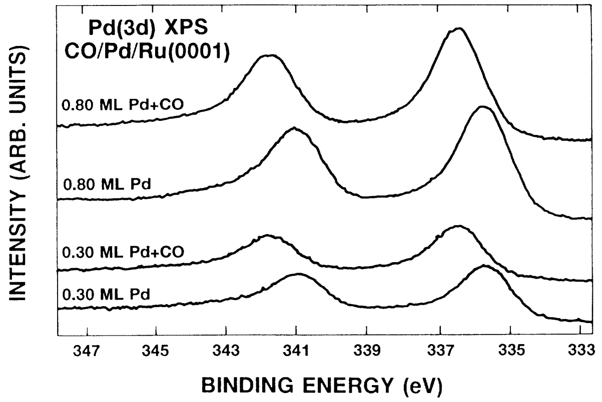

FIG. 10. XPS spectra of the Pd(3*d*) region for clean and CO-covered Pd/Ru(0001) systems. The Pd films were deposited at ~350 K and annealed to 500 K. The surface was then cooled to ~115 K and dosed with 10 L of CO.

the Pd($3d_{5/2}$) binding energy due to CO adsorption was found to be reversible. Upon CO desorption (anneal to 500 K) the Pd($3d_{5/2}$) binding energy returned to that value measured for the clean Pd/Ru system.

IV. DISCUSSION

The XPS results in Sec. III show that the atoms in a monolayer of Pd on Ru(0001) and Re(0001) have a higher Pd($3d_{5/2}$) binding energy than the surface atoms of Pd(100). This agrees with studies for $Pd_{1.0}$/W(110),[4] $Pd_{1.0}$/Mo(110),[5] and $Pd_{1.0}$/Ta(110),[13] which show an identical trend. Similarly, UPS data for a monolayer of Pd supported on Ta(110),[6] Nb(110),[7] and W(110) (Ref. 8) show Pd valence levels at higher binding energy than those of bulk Pd. A simple interpretation of these results is that the shifts in core and valence levels are due to initial-state effects, and a consequence of charge transfer from the Pd adlayer to the metal substrates. Indeed, work-function measurements for Pd/W(110) (Ref. 12) and Pd/Ru(0001) (Ref. 26) support the direction of charge transfer indicated by photoemission, and imply that charge transfer between Pd and the substrate should be larger on early transition metals. However, shifts in core-level binding energies must be interpreted with caution,[29] since these shifts may be due to changes in the screening of the core hole (final-state effects). Clearly additional experimental evidence is necessary to verify the charge transfer suggested by XPS and UPS. In an adsorbate-substrate bond consisting of a significant charge transfer component, it is expected that the larger the charge transfer, the stronger the cohesive energy of the bond. In good agreement with this expectation, results to be presented below indicate that the desorption temperature of the metal adlayer increases with an increase in the core-level shift. A second method for ascertaining the relative magnitude of the charge transfer between the metal adlayer and metal substrate is to monitor adsorption processes that depend markedly on the electron-donor properties of the adlayer. Two good examples of these kinds of processes are CO chemisorption ($CO_g \rightarrow CO_a$) and the dissociative adsorption of H_2 ($H_{2,g} \rightarrow 2H_a$). As we will see below, data obtained for these processes on Pd overlayers are consistent with the direction of charge transfer indicated by XPS and support a simple interpretation based on initial-state effects.

A comparison of the monolayer desorption temperature for Pd from the Ru(0001) and Re(0001) surfaces with those previously reported for the $Pd_{1.0}$/Ta(110) (Ref. 9) and $Pd_{1.0}$/W(110) (Ref. 11) systems is shown in Fig. 11(b). A monolayer of Pd on Ta(110) is found to have the highest desorption temperature (1540 K) with alloying occurring above temperatures of 600 K, while a Pd monolayer on Ru(0001) desorbs at only 1440 K. These data indicate that the less occupied the valence *d* band of the substrate, the stronger the Pd-substrate bond. It is noteworthy that Pd has a valence band almost fully occupied. Therefore electron-donor–electron-acceptor interactions between the adlayer and the substrate likely are responsible for the trend seen in Fig. 11(b). Furthermore, Ni and Pd are in the same column of the Periodic Table. A comparison of the desorption temperatures of Ni monolayers from Ta(110),[30] W(110),[31] Mo(110),[32,33] and Ru(0001) (Ref. 34) surfaces in Fig. 12(b) indicates the same general trend observed for Pd: the cohesive energy of the admetal-substrate bond increases as the fraction of empty states in the valence band of the substrate increases.

Interesting correlations also have been observed for supported monolayers of Cu.[35] The desorption temperatures of Cu monolayers from Ta(110),[36] Mo(110),[32] Re(0001),[35] Ru(0001),[37] and Rh(100) (Ref. 38) substrates are compared in Fig. 13(b). The strongest Cu-substrate bond occurs for the substrates on the extreme left- and

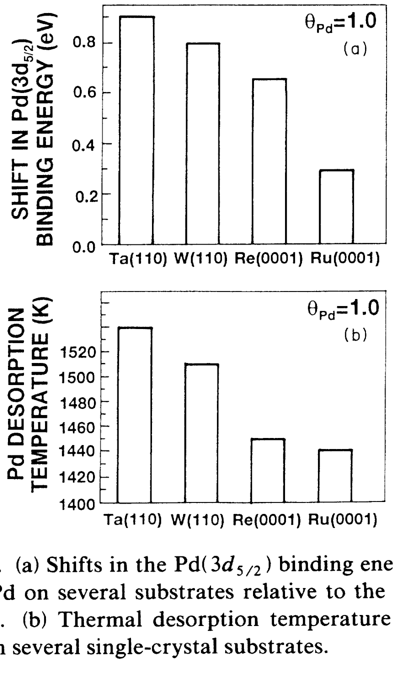

FIG. 11. (a) Shifts in the Pd($3d_{5/2}$) binding energy for monolayers of Pd on several substrates relative to the surface atoms of Pd(100). (b) Thermal desorption temperature of Pd monolayers from several single-crystal substrates.

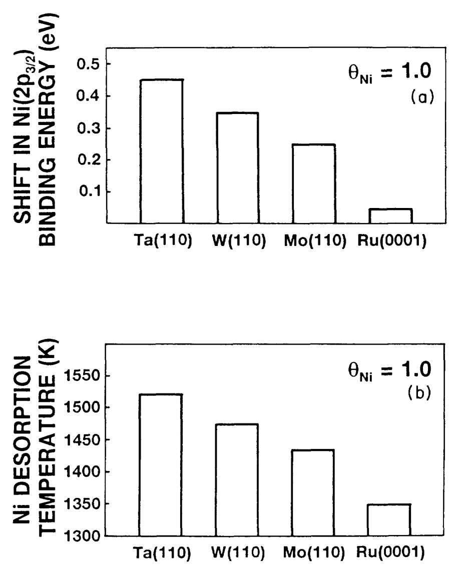

FIG. 12. (a) Shifts in the Ni($2p_{3/2}$) binding energy for a Ni monolayer on different surfaces with respect to Ni(100) surface atoms. (b) The desorption temperature for a monolayer of Ni atoms from different single-crystal surfaces.

right-hand sides of the transition series. A minimum in the desorption temperature occurs for the Cu/Re(0001) system. Cu has a 4*s* band that is only half occupied, and interacts strongly with metals in which the valence band is either nearly empty or nearly full.

The electronic perturbations of the Pd, Ni, and Cu adatoms can be determined using core-level shifts from XPS. It is found, in general, that Pd monolayers supported on early transition-metal substrates have a higher binding energy compared to the subsurface atoms of pure Pd. In contrast, the surface atoms of Pd(100) exhibit a Pd($3d_{5/2}$) binding energy 0.40 eV (Ref. 39) below that of subsurface Pd atoms. This reduction in binding energy is attributed to a decrease in the coordination number of the surface atoms that produces net charge transfer from the bulk to the surface.[29,41] To determine precisely the magnitude of the perturbation of various Pd monolayers, the Pd($3d_{5/2}$) binding energy of thick Pd films ($\Theta_{\text{Pd}} > 20$ ML in Figs. 2 and 8) can be referenced against the combined bulk plus surface peak of Pd(100) (see Fig. 14).[4] Using this method, the perturbation of a monolayer of Pd with respect to the surface atoms of Pd(100) is found to be +0.90, +0.80, +0.65, and +0.30 eV on the Ta(110),[13] W(110),[4] Re(0001), and Ru(0001) substrates, respectively [see Fig. 11(a)]. In all cases, the sign of the binding energy shift is consistent with charge transfer from the Pd overlayer to the substrate. In agreement with our results, recent UPS measurements for Pd monolayers on W(110),[8] Ta(110),[6] and Nb(110) (Ref. 7) indicate that there is a depletion of electronic density near the Pd Fermi level, and that the supported Pd exhibits a valence-band structure similar to that observed for noble metals. In contrast Pd multilayers and pure Pd exhibit photoemission spectra characterized by a large density of states near the Fermi level. A comparison of the surface core-level shifts from XPS with the desorption temperature of Pd monolayers in Fig. 11 indicates that there is an excellent correlation between the two measurements. Those systems with highest Pd-desorption temperatures correspond to those with the largest shifts in the Pd($3d_{5/2}$) binding energy.

The magnitude of the electronic perturbation (or strength of the admetal-substrate bond) is found to decrease as the transition-metal substrate "moves" from left to right in the Periodic Table. This trend can be explained by taking into consideration orbital mixing:[42] hybridization of the occupied states of Pd (the electron-rich metal) with the unoccupied levels of the substrate (the

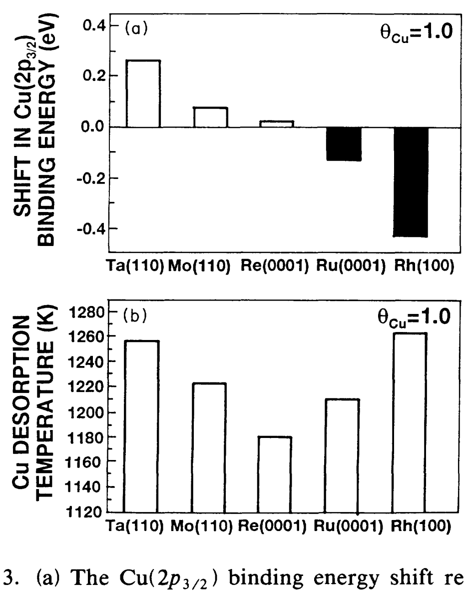

FIG. 13. (a) The Cu($2p_{3/2}$) binding energy shift relative to Cu(100) surface atoms for a Cu monolayer on several single-crystal surfaces. (b) Thermal desorption temperatures of a Cu monolayer from transition-metal surfaces.

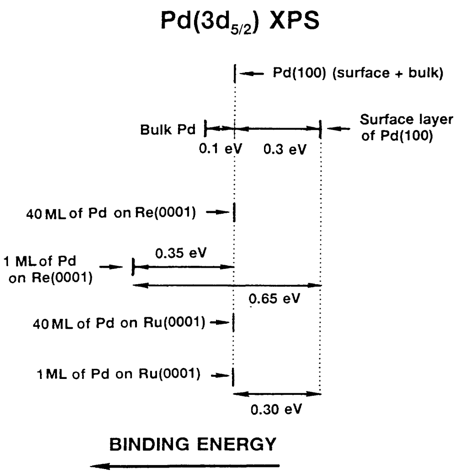

FIG. 14. Relative Pd($3d_{5/2}$) XPS binding energies of bulk Pd, the surface atoms of Pd(100) (Ref. 39), and a monolayer of Pd on Re(0001) and Ru(0001).

electron-poor metal) leads to a loss of Pd character in the occupied states and thus to a reduction in the electron density of Pd. Thus, as the fraction of empty levels in the valence band of the substrate decreases, the magnitude of the induced perturbation, via loss of Pd electron density, also decreases.

A comparison between the desorption temperature and the shift in the Ni($2p_{3/2}$) binding energy[20,43] for Ni monolayer systems in Fig. 12 shows the same general trend that is observed for the Pd overlayer systems. The largest interaction of the Ni overlayer is found for the substrate that has the least occupied valence *d* band. It is noteworthy that monolayers of Ni are perturbed to a lesser degree than are monolayers of Pd. One possible explanation for this difference between Ni and Pd is that the metallic radius of Pd (1.38 Å) is closer to that of the second- and third-row transition-metal substrates than is the radius of Ni (1.25 Å). A mismatch in the overlayer-substrate radii will likely result in less-efficient orbital overlap compared to a well-matched pair. This reduction in overlap between the appropriate overlayer-substrate orbitals should, in turn, inhibit the transfer of electronic charge within the bond.

In Fig. 13, data are presented for the Cu monolayer desorption temperatures and the shifts in the Cu($2p_{3/2}$) binding energy.[42,45] These data are clearly quite different from the analogous data for the Ni and Pd systems. Similar to the Ni and Pd systems, the Cu overlayers apparently transfer charge to the early transition metals (Ta, Mo). On the other hand, a Cu overlayer adsorbed onto a late transition metal (Ru, Rh) appears to withdraw electronic charge from the substrate. The electron-rich–electron-poor model[42] utilized to explain the Pd and Ni overlayer systems predicts this trend very well. It is noteworthy that Cu has a 4*s* valence band that is half occupied. Thus, when Cu is adsorbed onto transition metals with less than a half-occupied valence band, Cu acts as the electron-rich metal, donating charge to the substrate. Adsorbed onto a substrate with more than half-occupied valence band, Cu behaves as an electron-poor metal, accepting charge from the substrate. Finally, for a substrate which also has a half-occupied valence band (Re), the XPS results of monolayer Cu show essentially no perturbation.

The correlations in Figs. 11–13 indicate that the core-level shifts measured in XPS are mainly a consequence of initial-state effects. By comparing the TPD results of the Pd, Ni, and Cu monolayers with the XPS core-level shifts, it is clear that charge transfer is an important component of the cohesive energy of metal-metal bonds at a surface. Systems that show the strongest metal adlayer-metal substrate bonds also show the largest charge transfer between the overlayer and the substrate.

Another direct way to verify that the XPS core-level shifts are due to initial-state effects is by monitoring the ability of the metal overlayer to chemisorb CO. If the electronic properties of the metal adlayer are altered, one should also see a change in the chemical properties. In Fig. 15(b), TPD results of CO from the Pd$_{1.0}$/Ru(0001) and Pd$_{1.0}$/Re(0001) systems are presented along with those for the Pd$_{1.0}$/Ta(110),[9] Pd$_{1.0}$/W(110),[11] and Pd(100) (Ref. 10) systems. In these TPD spectra, it should be noted that the CO-desorption temperature for the overlayer systems is considerably lower than that observed for Pd(100). The extreme case is CO/Pd$_{1.0}$/Ta(110), which shows a reduction of 235 K in the CO-desorption temperature and a weakening of $\sim$15 kcal/mol in the strength of the Pd-CO bond. Comparing the Pd core-level binding energy shifts in Fig. 15(a) with the CO-desorption temperature shifts, a qualitative correlation is apparent. The Pd system with the lowest electron density shows the weakest Pd-CO bond, and vice versa. This correlation between the two sets of data can be easily explained in terms of the bonding mechanism of CO to metals.[48–54] From a thermodynamic viewpoint, CO-metal bonding is dominated by donation of electron density from the occupied valence bands of the metal into the empty CO $2\pi^*$ molecular orbitals (π backdonation).[50–54] The more π backbonding, the stronger the metal-CO bond. Transfer of electrons from Pd to the metal substrate reduces the ability of Pd to π backdonate to CO, thus decreasing the overall CO-metal bond strength. This implies that the separation between the occupied valence levels of Pd,

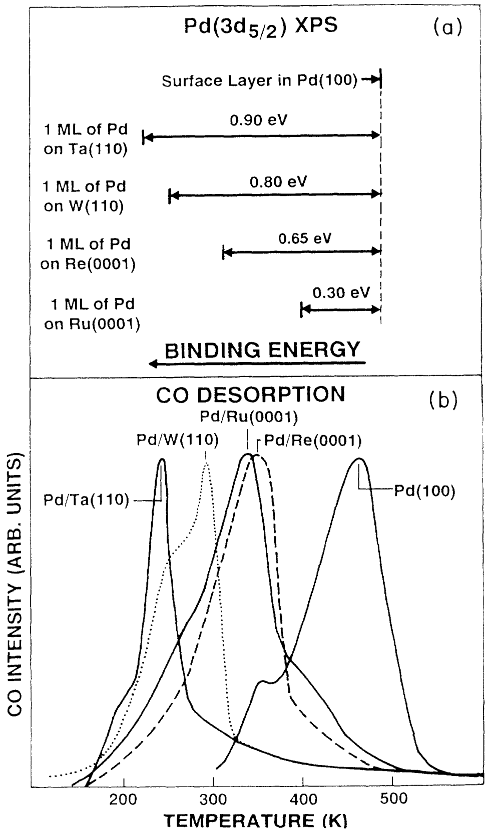

FIG. 15. (a) Relative Pd($3d_{5/2}$) XPS binding energies for surface atoms of Pd(100) and monolayers of Pd on Ta(110), W(110), Ru(0001), and Re(0001). The Pd($3d_{5/2}$) binding energies were measured on clean surfaces, without CO adsorbed. (b) CO-desorption spectra ($m/e=28$) for Pd$_{1.0}$/Ta(110), Pd$_{1.0}$/W(110), Pd$_{1.0}$/Re(0001), Pd$_{1.0}$/Ru(0001), and Pd(100).

E_{VB} below the vacuum level, and the empty $2\pi^*$ orbitals of CO, at ~1.8 eV above the vacuum level (Refs. 55–57), has increased for the Pd overlayer systems. A recent study has shown that changes in the work functions measured for overlayer films correlate with the binding energy shifts measured with XPS.[58] According to first-order perturbation theory,[59] an increase in the $E_{2\pi}$-E_{VB} separation results in a decrease in the heat of adsorption and in the Pd-CO bond strength. There is clearly a qualitative agreement between the implied charge density of the Pd overlayers and the desorption temperatures of CO from these surfaces.

For supported monolayers of Ni (Ref. 20) and Cu,[35,42] a correlation has been found similar to that displayed for Pd in Fig. 15. In general, an increase in core-level binding energy is accompanied by a reduction in the strength of the bond between CO and the supported metal monolayer, whereas the opposite is true for a reduction in the core-level binding energy. The direction of charge transfer between metals predicted by XPS agrees very well with the trends observed in CO TPD, indicating that the shifts in the surface core levels are initial-state effects.

A comparison of the electronic properties of the metal adlayers before and after CO chemisorption provides additional insight into the nature of the binding between metals. In Fig. 16(a), the CO-induced shifts and the CO-desorption temperatures are presented for Pd monolayers on Ta(100),[9,13] Re(0001), and Ru(0001), and for Pd(100).[10,60] Results are also shown in Fig. 16(b) for Cu(100) (Refs. 47 and 61) and Cu monolayers on Ru(0001),[46,62] Rh(100),[38,46] and Pt(111).[63,64] The XPS data were obtained in experiments similar to those described in Figs. 5 and 10. In all of these systems, the core-level shifts imply that the electron density about the Pd and Cu atoms is reduced after adsorption of CO.[65,66] The induced XPS shift yields qualitatively the relative charge transfer from the Cu or Pd atoms into the $2\pi^*$ orbitals of CO.[65,66] Our model predicts that π backdonation should occur to a lesser extent for those systems with the lowest CO-desorption temperatures. Indeed, the data in Fig. 16 indicate that there is qualitative agreement between the CO-desorption temperatures and the magnitude of the CO-induced shift. For Pd, charge transfer from the overlayer into the metal substrate leads to an electron deficient Pd admetal that is less efficient at π backdonation than the surface atoms of Pd(100). In contrast, Cu monolayers withdraw charge from the Rh and Pt substrates and are more efficient at π backdonation than the surface atoms of Cu(100).

Recent results of infrared absorption spectroscopy[13] (IRAS) and high-resolution electron energy loss[67] (HREELS) for CO on $Pd_{1.0}$/Ta(110) show a C-O stretching frequency at a much higher value than that observed on Pd(100). The reduced π backdonation leads to a smaller electron population in the antibonding $2\pi^*$ orbitals of CO and thus to a stronger C-O bond.

Studies reported in the literature[1,68] for the dissociative adsorption of H_2 on Pd overlayers also suggest that there is a charge transfer from the admetal to the substrate. In the dissociation of H_2 on metals, electron transfer from the surface into the σ^* antibonding orbital of the molecule plays a significant role in the breaking of the H-H bond, lowering the activation energy associated with the process.[69–71] Transition metals, such as pure Pd, are good electron donors, and dissociation of H_2 on these surfaces occurs readily at room temperature.[1] In contrast, no dissociation of H_2 is observed on $Pd_{1.0}$/Nb(110) under similar experimental conditions.[68] This reduction in reactivity of the supported Pd monolayer is probably a consequence of a decrease in the electron density of the adatoms. The behavior of $Pd_{1.0}$/Nb(110) is similar to that seen for noble-metal substrates,[1] surfaces that are poor electron donors and dissociate H_2 with difficulty due to a substantial activation barrier for H-H bond cleavage.[72]

The ability of a chemically bonded atom to attract electrons to itself is a measure of its electronegativity.[73–76] The results from XPS and CO TPD allow us to develop a system to qualitatively determine the electronegativity of metal atoms at a surface. This surface electronegativity is found to be quite different from the electronegativity seen for bulk atoms. The electronegativities for bulk transition metals increase from left to right in

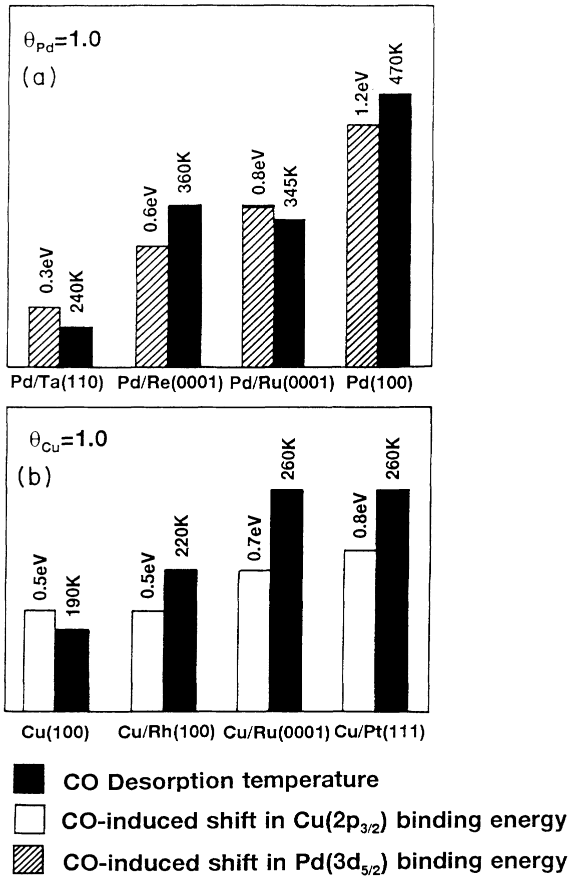

FIG. 16. (a) CO-desorption temmperature and CO-induced shift of the Pd($3d_{5/2}$) binding energy for Pd(100) and Pd monolayers on Ta(110), Re(0001), and Ru(0001). (b) Induced shift of the Cu($2p_{3/2}$) binding energy from CO adsorption, and desorption temperature of CO for Cu(100) and Cu monolayers on Ru(0001), Rh(100), and Pt(111).

the transition series[77] and then drop for Cu, Ag, and Au. For three-dimensional alloys, charge is expected to flow from the element on the left to the element on the right of the Periodic Table. Mössbauer experiments and self-consistent density-functional calculations for alloys involving Ta, W, Au, and Pt (Refs. 78–81) have shown this trend to be true. The charge transfer measured with XPS and CO TPD allows for the determination of the electronegativities of Pd, Ni, and Cu with respect to the transition-metal substrates investigated. Qualitatively we have determined the electronegativities to be as follows:

$$\mathrm{Ta}(110) > \mathrm{W}(110) > \mathrm{Mo}(110) > \mathrm{Re}(0001) \approx \mathrm{Cu} > \mathrm{Ru}(0001) > \mathrm{Rh}(100) > \mathrm{Ni} > \mathrm{Pd}\ ;$$

increasing from right to left in the transition series. This trend is exactly opposite to that observed for bulk alloys. A complete theoretical understanding for the differences between bulk and surface electronegativities is lacking; however, the anisotropic character of the surface atoms is clearly a key contributing factor.[35]

Variations in the coordination number of an atom or in the geometrical arrangement of its neighbors can produce changes in its orbital hybridization that modify its electronegativity.[35,74–76] For pure metals, photoemission studies[29] indicate that surface and bulk atoms have quite different electronic properties. In this sense, it is not surprising that surface atoms behave chemically in a different way than bulk atoms.

V. CONCLUSIONS

(1) The electronic and chemical properties of monolayers of Pd, supported on transition-metal substrates, *are* different from those found for Pd(100). The largest perturbations are found for bimetallic systems that involve a combination of an electron-rich and an electron-poor metal.

(2) Charge transfer is an important component in surface metal-metal bonds that involve dissimilar elements. Charge flows toward the metal with the larger fraction of empty states in its valence band. The larger the charge transfer, the stronger the cohesive energy of the overlayer-substrate bond.

(3) Bulk electronegativities cannot be used to predict charge transfer for metal atoms on a transition-metal substrate. For transition-metal surfaces, the electronegativity increases from right to left in the Periodic Table.

(4) There is excellent agreement between the electronic properties of bimetallic systems and their ability to chemisorb CO. The core-level shifts produced by CO adsorption are an excellent indicator of the ability of the bimetallic system to transfer charge to the $2\pi^*$ orbitals of CO.

ACKNOWLEDGMENTS

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences and the Robert A. Welch Foundation.

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