

Electron Donor-Electron Acceptor Interactions in Bimetallic Surfaces: Theory and XPS Studies

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The electronic interactions in Pd/Mo(110), Pd/Ru(0001), and Cu/Mo(110) have been examined by means of X-ray photoelectron spectroscopy (XPS). The shifts in core-level binding energies indicate that adatoms in a monolayer of Cu or Pd are electronically perturbed with respect to surface atoms of Cu(100) or Pd(100). By comparison of these results with those previously presented in the literature for adlayers of Pd or Cu, a simple theory is developed that explains the nature of electron donor-electron acceptor interactions in metal overlayers: formation of surface metal-metal bonds leads to a gain in electrons by the element initially having the larger fraction of empty states in its valence band. This behavior is contrary to that predicted by bulk electronegativities and observed in bulk alloys, indicating that the electronegativities of the surface atoms are substantially different from those of the bulk.

I. Introduction

In recent years, the electronic, chemical, and catalytic properties of bimetallic surfaces generated by vapor-depositing one metal onto a crystal face of a second metal have been the focus of considerable attention.¹⁻³ This interest has been motivated by the relevant role that bimetallic surfaces play in areas of catalysis, electrochemistry, and microelectronics. The main objective is to obtain a fundamental understanding of phenomena that accompany the formation of surface metal-metal bonds and see how these phenomena modify the properties of the elements in the bimetallic system.

Previous UPS and XPS studies for submonolayer films of Pd supported on W(110),^{4,5} Ta(110),^{6,7} Nb(110),⁸ and Re(0001)⁹ show binding energies for the core and valence levels of the adatoms that are considerably larger than those seen for bulk Pd. In contrast, XPS results for 1 monolayer (ML) of copper on Rh(100), Cu_{1.0}/Rh(100), or on Pt(111), Cu_{1.0}/Pt(111), show Cu(2p_{3/2}) peak positions that are at lower binding energy than that of bulk Cu.^{10,11} An excellent correlation has been found between the changes in core-level binding energies and variations in the ability of the supported films to adsorb CO.^{9a,12} Supported monolayers of Pd and Cu show unique chemisorption properties toward CO. For example, TPD data indicate a much lower (~180 K) CO desorption temperature from Pd_{1.0}/W(110) than from Pd(100).^{12,13} On the other hand, for CO adsorption on Cu_{1.0}/Rh(100) an increase of ~70 K in the CO TPD maximum with respect to the peak maximum on Cu(100) has been observed.^{12,14} All this evidence indicates that the supported Cu or Pd adatoms are electronically perturbed and that the effects of the metal overlayer-metal substrate interaction can be very different from one bimetallic system to another.

In this Letter we present XPS data for ultrathin films of Cu or Pd supported on Mo(110) and Ru(0001). By comparison of these results with those previously presented in the literature for adlayers of Pd, Ni, and Cu, a simple theory evolves that explains the nature of many electronic perturbations in bimetallic systems. The theory interprets satisfactorily trends observed in CO chemisorption and in XPS data and provides a conceptual frame to qualitatively predict electronic changes that will appear as a consequence of bonding two dissimilar metals.

II. Experimental Section

The experiments were carried out in an ultrahigh-vacuum chamber (base pressure <4 × 10⁻¹⁰ Torr) equipped with capabilities for AES, XPS, LEED, and TPD.⁴ Detection was normal to the surface in XPS and AES. The X-ray photoelectron spectra were recorded with Al K α radiation. The variations in the binding energies of the Cu(2p) and Pd(3d) regions were determined by

referencing against the 3d_{5/2} peak of Ru(0001) or Mo(110) and have an experimental error of ± 0.03 eV.

The surfaces were cleaned following procedures reported in the literature.¹⁵ Cu (or Pd) deposition was performed by resistively heating a W filament wrapped with a high-purity Cu (or Pd) wire. The coverages were determined by TPD area and AES analysis.^{16,17} All admetal coverages are reported with respect to the number of substrate surface atoms (Ru(0001), 1.57 × 10¹⁵ atoms/cm²; Mo(110), 1.43 × 10¹⁵ atoms/cm²). One Cu or Pd atom per substrate surface atom corresponds to θ_{Cu} or θ_{Pd} equal to 1.0.

III. Results

1. Pd/Mo(110) and Pd/Ru(0001) Systems. Figure 1 shows representative spectra of the Pd(3d) XPS region for various coverages of Pd on Mo(110) and Ru(0001). In both bimetallic systems, there are not any extra features or changes in line shape with increasing Pd coverage. For Pd/Mo(110), a clear decrease in core-level binding energy can be observed: the Pd(3d_{5/2}) peak position shifts from 336.25 eV for $\theta_{Pd} = 0.65$ and 1.0 ML to 335.65 eV for $\theta_{Pd} = 20$ ML. In contrast, the Pd/Ru(0001) system shows identical binding energies (335.65 eV) for films with 1 and 15 ML of Pd.

For adsorbate coverages (film thicknesses) in excess of 1 ML, the X-ray photoelectron spectra of Figure 1 represent a product

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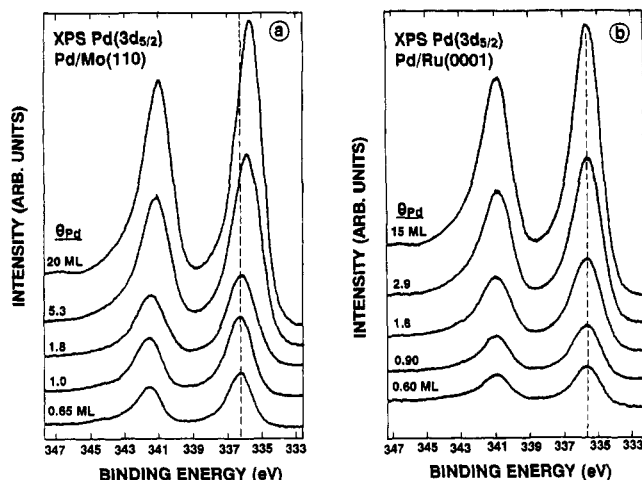


Figure 1. Pd(3d) XPS spectra of Pd/Mo(110) (part a) and Pd/Ru(0001) (part b) as a function of Pd coverage. Pd was vapor-deposited at a sample temperature of ~ 350 K. The surfaces were annealed to 500 K before acquiring the spectra.

of a combination of electrons emitted from subsurface and surface atoms. If we compare the combined Pd(3d_{5/2}) peak of 40 ML of Pd on Mo(110) to that of Pd(100) (see Figure 2a), a difference of approximately 0.9 eV is obtained between the Pd(3d_{5/2}) binding energy of a monolayer of Pd supported on Mo(110) and that of the surface atoms of Pd(100). The corresponding value for Pd_{1.0}/Ru(0001) is 0.3 eV. For Pd_{1.0}/Mo(110) and Pd_{1.0}/Ru(0001), the XPS results are consistent with a model in which the electron density of the Pd adatoms is smaller than that of the surface atoms of Pd(100). In this model, electrons are transferred from occupied orbitals of the Pd monolayers into empty electronic states of the substrate (molybdenum or ruthenium). An identical phenomenon has been observed for Pd films supported on W(110),⁴ Re(0001),⁹ and Ta(110).^{7,9}

2. Cu/Mo(110) and Cu/Ru(0001) Systems. Previous XPS studies for Cu/Ru(0001)^{10,12} indicate that the Cu(2p_{3/2}) binding energy increases with film thickness, reaching a constant value at ~ 5 ML. The atoms in a pseudomorphic monolayer of Cu on Ru(0001) are electronically perturbed with respect to the bulk atoms of pure Cu, appearing ~ 0.35 eV at lower binding energy in the Cu(2p_{3/2}) XPS spectrum. Figure 3 shows XPS spectra acquired after vapor-depositing films with different Cu coverages on Mo(110). The Cu(2p_{3/2}) peak position found for 1 ML of Cu is ~ 0.1 eV smaller than that for 30 ML of Cu (932.9 eV). Figure 2b compares the Cu(2p_{3/2}) binding energies of supported Cu monolayers with those of bulk and surface atoms of Cu(100). The relative magnitude of the electronic perturbations is different from that observed for the Pd adlayers (Figure 2a). For the Cu systems, the largest shift in core-level binding energy is found for Cu_{1.0}/Ru(0001). In contrast for the Pd systems, the strongest electronic perturbation is seen for Pd_{1.0}/Mo(110).

IV. Discussion

The results of section III.1 show Pd(3d_{5/2}) binding energies for submonolayer films of Pd that are considerably larger than the corresponding value for the top layer of Pd(100). An identical trend has been observed previously for the core and valence levels of supported monolayers of Pd on W(110),^{4,5} Ta(110),^{4,7} Nb(110),⁸ and Re(0001).⁹ Results of UPS and XPS for Pd/W(110) and Pd/Ta(110) indicate that the shifts in Pd core levels track the corresponding shifts in Pd valence levels, with the levels of the supported Pd monolayers appearing always at higher binding energy than those of bulk Pd.^{1,4,7}

The top part of Figure 4 illustrates how the difference in Pd(3d_{5/2}) binding energy between a monolayer of supported Pd and the surface atoms of Pd(100) varies with metal substrate. In all the cases, the direction of the electronic perturbation for the Pd adatoms is consistent with a model in which there is charge transfer from the overlayer into the substrate. The magnitude of the electronic perturbation increases as the transition-metal substrate

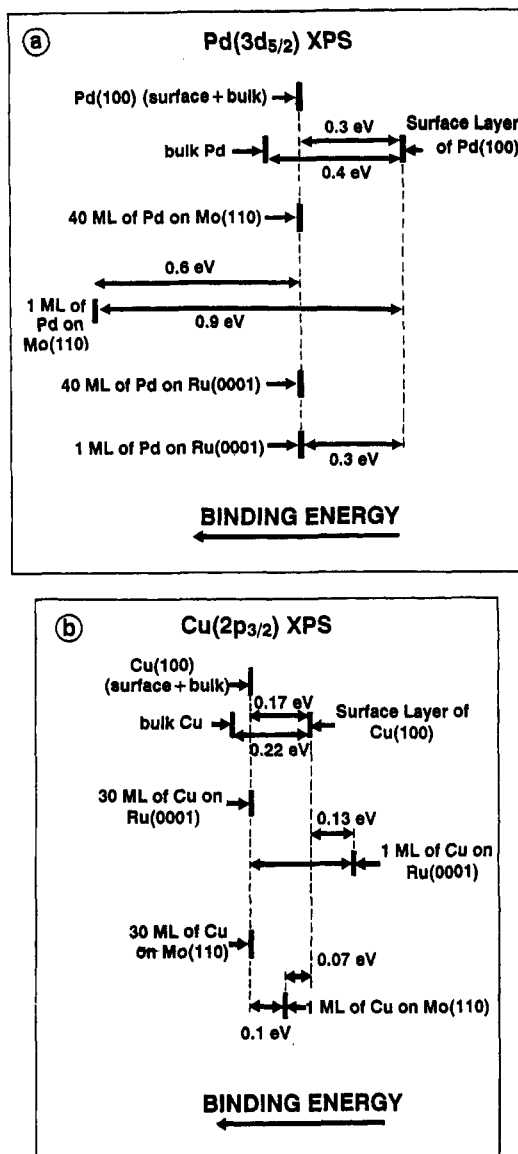


Figure 2. (a) Relative Pd(3d_{5/2}) XPS binding energies of bulk Pd, the surface atoms of Pd(100), and monolayers of Pd on Mo(110) and Ru(0001). (b) Relative Cu(2p_{3/2}) XPS binding energies of bulk Cu, the surface atoms of Cu(100), and monolayers of Cu on Mo(110) and Ru(0001).

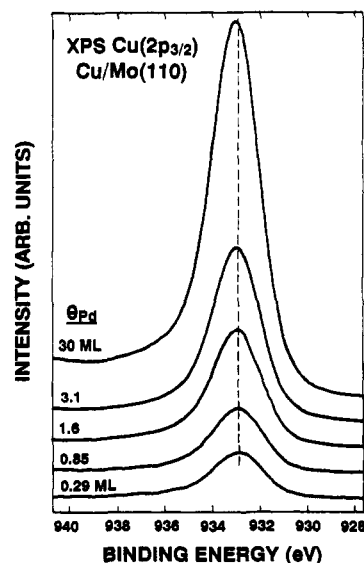


Figure 3. Cu(2p_{3/2}) XPS spectra of Cu/Mo(110) as a function of Cu coverage. Cu was vapor-deposited at a sample temperature of ~ 350 K. The surfaces were annealed to 500 K before acquiring the spectra.

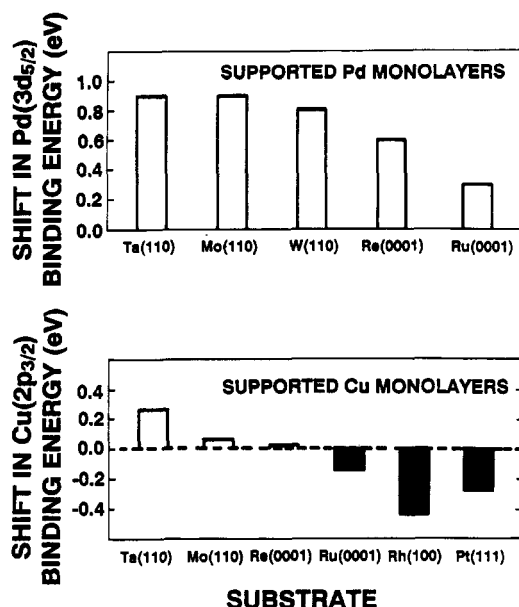


Figure 4. Top: difference in Pd(3d_{5/2}) XPS binding energy between 1 ML of Pd and the surface atoms of Pd(100) as a function of metal substrate. The results for Pd_{1.0}/Mo(110) and Pd_{1.0}/Ru(0001) are compared with data for Pd monolayers on Ta(110),⁹ W(110),⁴ and Re(0001).⁹ Bottom: difference in Cu(2p_{3/2}) XPS binding energy between 1 ML of Cu and the surface atoms of Cu(100) as a function of metal substrate. The results for Cu_{1.0}/Mo(110) and Cu_{1.0}/Ru(0001) are displayed with data for Cu monolayers on Ta(110),⁹ Re(0001),²¹ Rh(100),¹⁰ and Pt(111).⁹

"moves" from the right to the left in the periodic table. An identical trend was observed for Ni adlayers.¹⁸ For pseudomorphic Pd adlayers the surface atomic density follows the order Ta(110), 1.30×10^{15} atoms/cm² < W(110), 1.42×10^{15} atoms/cm² \approx Mo(110), 1.43×10^{15} atoms/cm² < Re(0001), 1.54×10^{15} atoms/cm² < Ru(0001), 1.57×10^{15} atoms/cm². It appears that the systems with larger Pd-Pd bond distances (i.e., weaker Pd-Pd interactions) have stronger Pd-substrate interactions, and as a consequence they show larger electronic perturbations. For late transition metals, an increase in surface atomic density (i.e., effective coordination number) usually leads to an increase in core-level binding energy.^{19,20} This is not observed in Figure 4, stressing the importance of the adlayer-substrate interactions.

Results of photoemission for Cu_{0.6}/Pt(111)¹¹ show that the Cu(2p_{3/2}) level and Cu(3d)-band centroid of the Cu overlayer are at lower binding energy than the corresponding values for the bulk and surface atoms of Cu(100). Our results of section III.2 indicate that supported Cu monolayers can have binding energies that are above or below that of the atoms in the top layer of Cu(100). The bottom part of Figure 4 shows how the difference in Cu(2p_{3/2}) binding energy between a monolayer of supported Cu and the surface atoms of Cu(100) depends on metal substrate. The XPS data are consistent with a model in which Cu atoms supported on metals in the right side of the periodic table have electron densities larger than that of the surface atoms in Cu(100). Likewise, an opposite phenomenon is observed for Cu atoms over metals in the left side of the periodic table. In general, the magnitude of the electronic perturbation is bigger for substrates at the extremes of the periodic table. For pseudomorphic Cu monolayers the surface atomic density follows the sequence Ta(110) < Rh(100), 1.38×10^{15} atoms/cm² < Mo(110) < Pt(111), 1.51×10^{15} atoms/cm² \approx Re(0001) < Ru(0001). This ordering agrees well with the trends found in the bottom part of Figure 4. Again, it appears that the systems with the largest adatom-

adatom bond distances have the strongest overlayer-substrate interactions.

In order to fully understand the trends observed in Figure 4, it is necessary to have very detailed quantum-mechanical information about the bonding mechanism between the Cu or Pd overlayers and the metal substrates. Such information is not available at the present time. However, a simple model that explains the trends in Figure 4 evolves by considering the type of metals present in the bimetallic systems. The strongest electronic perturbations are found for systems that involve a combination of a metal with an almost fully occupied valence band and a metal with a valence band more than half empty. It appears that formation of a surface metal-metal bond generally leads to a gain in electron density by the element initially having the larger fraction of empty states in its valence band. The direction of electron transfer can be easily understood in terms of orbital mixing: hybridization of the occupied states of an electron-rich metal A with the unoccupied levels of an electron-poor metal B leads to a loss of A character in the occupied states and hence a reduction in the electron density on metal A.

For supported monolayers of Pd (electron-rich admetal) the magnitude of the perturbations induced by the loss of electron density increases as the fraction of empty levels in the valence band of the metal substrate increases: Ru < Re < W < Ta. Cu has a 4s valence band that is half empty. Therefore, supported Cu can act as an electron donor or electron acceptor depending on the relative fraction of empty states in the valence band of the metal substrate. For Re, the 5d valence band is also half empty, and as a consequence only a minor perturbation is observed for the Cu_{1.0}/Re(0001) system (Figure 4 and ref 21). Adsorption of Cu on metals to the left of Re (substrates with valence band more than half empty) produces a reduction in the electron density of the adatoms. On the other hand, when Cu is deposited on metals in the right side of the periodic table (elements with valence bands more than half occupied), electrons flow from the substrate into the 4s band of the admetal.

It can be expected that the electronic perturbations described above will modify the chemical properties of the metal overlayers. An excellent correlation has been found between the changes in core-level binding energies and variations in the ability of the supported films to adsorb CO.^{1,9a,12} This correlation can be easily explained in terms of the theory outlined in the previous paragraphs. TPD data indicate CO desorption temperatures from Pd_{1.0}/Ta(110) (~ 250 K⁹), Pd_{1.0}/W(110) (~ 300 K¹³), and Pd_{1.0}/Ru(0001) (~ 330 K) that are much lower than that from Pd(100) (~ 480 K²²). According to our theory, the electron density of supported monolayers of Pd is smaller than that of the surface atoms of Pd(100). A partial positive charge on the Pd adatoms is consistent with a reduction in their ability to coordinate CO via π -back-bonding, producing a weaker Pd-CO bond on the supported monolayers compared to Pd(100). Our theory predicts that the electron density and ability to π -back-donate of the Pd surface atoms will follow the sequence Pd_{1.0}/Ta(110) < Pd_{1.0}/W(110) < Pd_{1.0}/Ru(0001) < Pd(100). This trend is in excellent agreement with the TPD results.

For monolayers of Cu deposited on electron-rich metals (Ru, Rh, and Pt), the theory predicts an enhancement in the electron density and π -back-bonding capacity of the Cu adatoms with respect to the surface atoms of Cu(100). This prediction agrees very well with TPD data that show larger (30–70 K) CO desorption temperatures from the supported Cu monolayers than from Cu(100).^{9,12,14} Adsorption of CO on Cu films induces a large increase in the Cu(2p_{3/2}) XPS binding energy, in part, due to π -back-donation.^{10,21,23} Figure 5 shows how the CO-induced shift in Cu(2p_{3/2}) peak position (measured after saturating the Cu surfaces with CO at 100 K) changes with metal substrate. For

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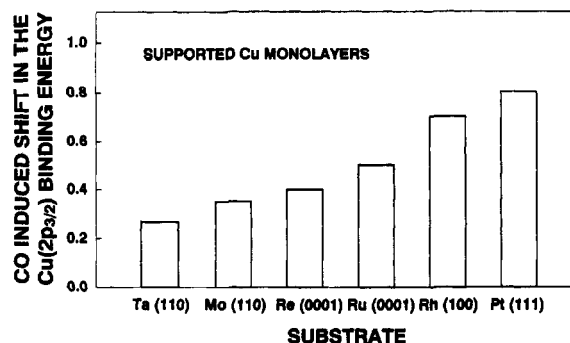


Figure 5. CO-induced shifts in Cu(2p_{3/2}) peak position (measured after saturating the Cu surfaces with CO at 100 K). The results for Cu_{1.0}/Mo(110) and Cu_{1.0}/Ru(0001) are compared with data for Cu monolayers on Ta(110),⁹ Re(0001),²¹ Rh(100),¹⁰ and Pt(111).⁹

the surface atoms of Cu(100) a shift of ~0.5 eV has been reported.²⁴ In Figure 5, the CO-induced shift increases when the metal substrate "moves" from left to right in the periodic table. This trend can be attributed to an increase in the ability of the Cu adatoms to π -back-donate and is consistent with the predictions of our theory.

The theory described above, based on a simple model of electron transfer between metals with a dissimilar fraction of empty states in their valence bands, explains satisfactorily trends in XPS and CO chemisorption data for bimetallic surfaces. In many aspects, the behavior observed for the two-dimensional metal overlayers is different from that expected for bulk metals. In different scales of electronegativity for bulk transition metals,²⁵ the electronegativity increases from left to right in the periodic table. In three-dimensional metal alloys, charge is expected to flow from the element in the left to the element in the right of the periodic table.²⁵ For example, Mössbauer isomer shift results for Au (or Pt) alloys show net charge transfer from metals with low bulk electronegativity like Ta and W toward Au (or Pt).^{26,27} Identical results are found in self-consistent density functional calculations for Pt-Ta, Pt-W, Au-Ta, and Au-W bulk alloys.^{27,28} In contrast, the results presented above for the Pd_{1.0}/Ta(110), Pd_{1.0}/W(110), and Cu_{1.0}/Ta(110) systems are consistent with charge transfer from Pd and Cu (elements with large bulk electronegativity) toward Ta and W (elements with low bulk electronegativity).

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In order to understand the charge transfers in Figure 4, one must compare the electronegativities of the two-dimensional metal overlayers with the electronegativities of the surface atoms in the metal substrates. These sets of electronegativities are not available at the present time. However, experimental evidence indicates that they are very different from bulk electronegativities. For a metal, the atomic ionization potential and electron affinity differ considerably from the work function of the bulk solid.²⁹ Therefore, it is not surprising when a two-dimensional overlayer behaves in a different way than a three-dimensional solid. Results of XPS show core-level binding energies for surface metal atoms that are shifted with respect to those of the bulk atoms.^{19,20} The shifts are a consequence of differences in charge density.¹⁹ For d bands more than half full (right of periodic table), the surface atoms acquire a negative charge relative to the bulk (less electronegative) and the surface core levels shift to smaller binding energy. On the other hand, for d bands less than half full (left of the periodic table), the surface atoms are electron deficient with respect to the bulk (more electronegative), showing core-level shifts toward larger binding energy. Our results clearly demonstrate the expected different electronegativities for bulk and surface atoms. Furthermore, trends reported for relative bulk electronegativities²⁵ are *not* valid for surface electronegativities. As indicated above, in early transition metals the surface atoms are more electronegative than the bulk atoms, while the contrary is seen for late transition metals. For example, the results of Figure 4 indicate that the top layer of Ta(110) can be more electronegative than Pd or Cu.

V. Conclusions

Cu and Pd atoms are electronically perturbed when supported on single-crystal surfaces of transition metals. In general, the perturbations cannot be explained by using differences in bulk electronegativities but rather can be understood by considering the special electronegativity of the surface atoms. The electron donor–electron acceptor interactions that occur in these bimetallic systems have been explained in terms of a simple theory: formation of a surface metal–metal bond generally leads to a gain in electron density by the element having the larger fraction of empty states in its valence band. This behavior is contrary to that observed in bulk alloys, in which electrons flow from the electron-poor metal (left of periodic table, low bulk electronegativities) into the electron-rich metal (right of periodic table, large bulk electronegativities).

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