

Core-electron binding energies of adsorbed metallic monolayers: Au/Ag(111)

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Born-Haber cycles which relate core-electron binding energies of adsorbed isolated atoms and monolayers to adsorption enthalpies and monolayer cohesive energies are used to interpret the measured shifts for Au on Ag, Au, and Pt substrates and to deduce the cohesive interaction within the adlayer. For one monolayer of Au on Ag(111) the core-electron binding-energy shift is negative, but smaller in magnitude than that of surface atoms on bulk gold. The $5d$ band of the Au monolayers is, however, significantly narrower than that of the first monolayer on bulk gold, but not as much as expected on the basis of the reduced gold coordination number.

INTRODUCTION

The connection between the cohesive energies of solids and the core-electron binding energies in the bulk and at the surface has been elucidated by recent studies based on Born-Haber cycles.^{1,2} In the present work we extend these studies to interpret the core-electron binding energies in metal adsorbate atoms and monolayers on metallic substrates. Such adsorbed atoms usually form islands or other aggregates. As a result, measured core-electron binding energies normally contain contributions from both the adsorption energy on the surface and the cohesive energy within the aggregate. Using empirical adsorption enthalpies for isolated atoms on metallic substrates,³ we obtain a measure of the lateral interaction in adsorbed monolayers.

We consider Au layers grown epitaxially on Ag(111) substrates which exhibit layerwise growth,⁴ and compare the results with those of the first monolayer of the Au(111) surface itself,^{5,6} as well as with data for Au on Pt(111).⁷ Although the emphasis here is on properties of adsorbed monolayers, we will occasionally digress to consider multilayers.

EXPERIMENTAL DETAILS

The gold overlayers on Ag(111) used in this study were grown at room temperature by slow deposition of Au from a Knudsen cell onto (111)-oriented silver films supported on mica substrates. The Ag substrates had been sputtered and annealed until a satisfactory (1×1) low-energy electron diffraction (LEED) pattern was obtained. Deposition rates were monitored with a quartz-crystal microbalance, and checked against the attenuation of the Ag $3d$ signal from the substrate, using a 19-Å escape depth for Au and the appropriate take-off angle. The deposited gold did not have noticeable effect on the LEED pattern, confirming that the growth was epitaxial. Earlier studies⁴ have shown that the growth is layer by layer and that diffusion into the bulk is negligible at room temperature. (Rapid grain boundary diffusion of Ag through a Au overlayer has been observed at high gold coverage,⁸⁻¹⁰ but data from that regime are not considered in this report.) The resulting samples were introduced into a Hewlett-

Packard HP-5950A ESCA (electron spectroscopy for chemical analysis) spectrometer without exposure to higher pressure. X-ray photoemission spectra of the Ag $3d$, Au $4f$, and valence-band regions were then recorded. Wide scans and spectra of the C $1s$ and O $1s$ regions, taken to monitor surface conditions, showed that contaminants remained below 3% of a monolayer. All core-electron binding energies are referenced to the Fermi edge of the silver substrate, which was determined by least-squares fitting.

The contribution of the Au overlayer to the valence band was determined by subtracting a suitably attenuated spectrum of a clean Ag substrate. The attenuation was determined from the strengths of the Ag $3d$ core-electron spectra, on the assumption that the $3d$ and $4d$ spectra are affected to the same extent by the Au overlayer. A correction for the change in escape depth with kinetic energy had only a minor effect on the result of the subtraction because of the weak attenuation produced by a single monolayer. There are then no adjustable parameters in the subtraction. Implicit in this procedure is the assumption that the signal from the Ag substrate is not significantly altered by the Au overlayer. Any change should be confined to the outermost Ag layer which contributes ~20% of the signal. Covering the Ag with gold should make the silver surface layer more bulklike, increasing the width of the d band of the outer layer. Based on the magnitude of the surface-atom core-level shift of Ag,⁵ the modification of the Ag $4d$ band at the surface should be relatively small. The errors introduced by such changes should be concentrated near the edges of the Ag d band. Fortunately, the upper edge of the Au $5d$ band lies between the upper edge of the Ag $4d$ band and the Fermi level, and is reproduced without distortion.

RESULTS AND DISCUSSION

Valence-band spectra of the overlayer system with a coverage of approximately 1 monolayer (ML) of gold and of the Au overlayer, obtained by subtraction, are shown in Fig. 1. For comparison the spectra of a clean Ag substrate and a polycrystalline Au film are also shown. Essentially identical results were obtained for the Au $5d$

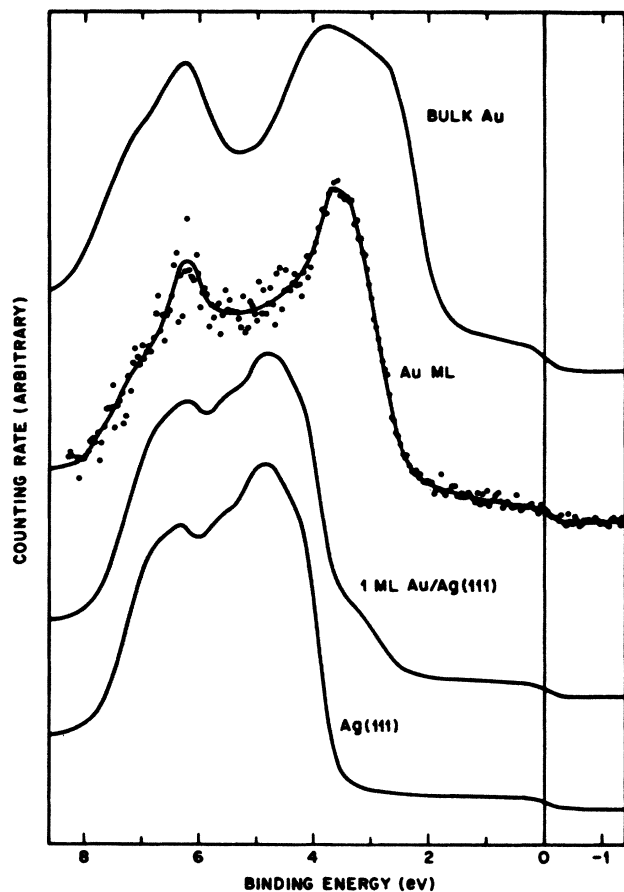


FIG. 1. Valence-band x-ray photoemission spectra of a clean Ag(111) substrate, and of a substrate covered by 1 monolayer (ML) of gold. The contribution of the Au overlayer is isolated by subtracting the contribution of the Ag substrate. For comparison the spectrum of a polycrystalline gold film is also shown.

band for all coverages below 1 ML. This confirms that the gold is mobile on the surface and rapidly aggregates into two-dimensional islands.

The Au $5d$ band structure of the monolayer is much narrower than that of bulk Au, or even that of the first monolayer on bulk Au.⁵ The shift with coverage of the upper edge of the Au $5d$ band is shown in Fig. 2. The lower edge coincides with that of the Ag d band, and does not exhibit a pronounced shift. The resulting bandwidth is in qualitative accord with a simple tight-binding s -band model which relates the width to the square root of the coordination number.¹¹ If the Au $5d$ -band width were determined by the number of Au neighbors, then the ratio of the d -band widths of the Au overlayer to that of bulk Au would be 0.71, while the corresponding ratio for the first atomic layer of bulk Au would be 0.87. The experimental width ratios are 0.78 and 0.92, indicating that this model does not account quantitatively for the behavior of the d band of a noble metal. A similar narrowing can also be seen in the uv photoemission data of Williams *et al.*¹² Band-structure calculations, are needed for a full-interpretation of these observations.

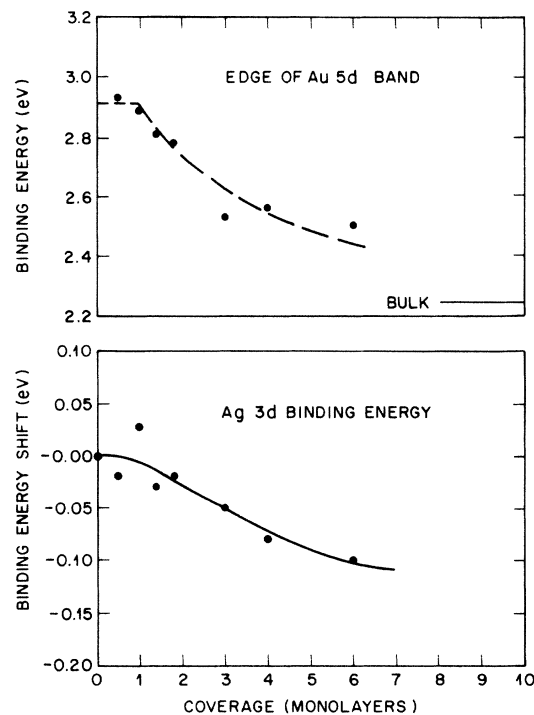


FIG. 2. Coverage dependence of the location of the upper edge of the $5d$ band of the Au overlayer, and of the $3d_{5/2}$ core-electron binding energy of the Ag substrate.

The spectra of the Ag $3d$ lines from a clean and a Au-covered substrate are shown in Fig. 3. The regions of the Ag surface plasmon are vertically enlarged to demonstrate the attenuation of the plasmon by the metallic overlayer, as previously reported.¹³ In this more detailed study we found that an adsorbed monolayer decreases the plasmon intensity by only 10% or 15% and that complete attenuation requires at least 6 ML.

The other interesting observation in Fig. 3 is that the Ag $3d$ core-electron binding energy decreases at the higher gold coverages. The shifts of the individual Ag layers were not resolved, and line broadening was minimal. The coverage-dependent shifts are shown in the lower half of Fig. 2. At a coverage of 1 ML the Ag exhibits no measurable shift, indicating weak electronic interaction between substrate and adsorbate. The shift observed at higher coverage has the wrong sign to be explained by the destruction of the negative Ag surface-atom core-level shift by the overlayer. Since the Ag surface-atom core-level shift is -0.08 eV,⁵ its removal produces only a small net *positive* shift when averaged over the layers that contribute to the $3d$ spectrum. Since the observed negative shift of the Ag $3d$'s becomes appreciable only after the second monolayer of Au has been deposited, i.e., after the gold develops normal metallic properties,¹⁴ one can relate the shift to the redistribution of charge at the interface expected on the basis of the difference in work functions. Electronic charge will flow from the Ag substrate to the Au overlayer resulting in an upward bending of the Ag bands at the interface. This accounts for the observed decrease in core-electron binding energy, provided the shift is greater than the change in

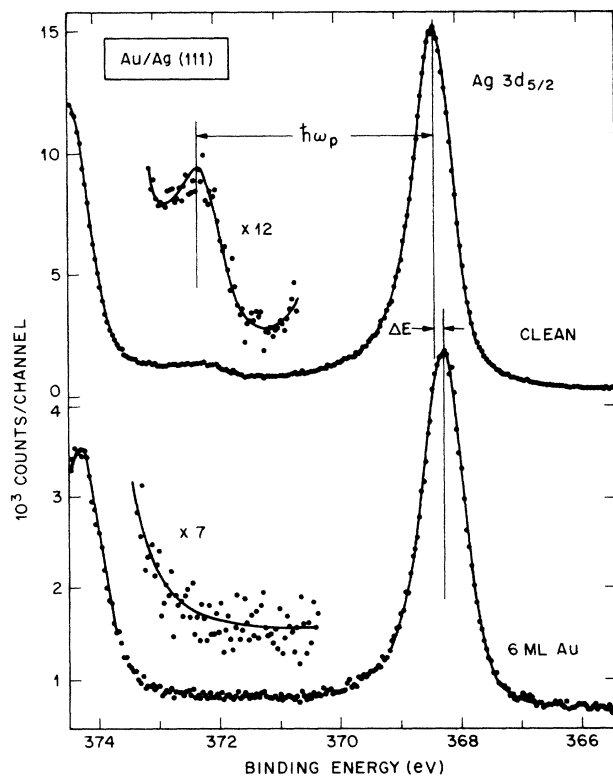


FIG. 3. The Ag 3d photoemission spectra of a clean Ag(111) substrate, and of a substrate covered by ~ 6 ML of Au. The enlarged regions show the silver surface plasmon.

the Coulomb coupling between the Ag core and conduction electrons, which produces a shift toward greater binding energy. In a system with low-density-of-states bands like those of graphite, this condition is readily satisfied.¹⁵ In view of the negative shift from Ag to Ag₂O, it should also be met in silver.

Turning now to the Au monolayer, we note first of all that the Au core-electron binding-energy shift is negative. Since the shift of Au in Au-Ag alloys is in a positive direction,¹⁶ the observation of a negative shift provides confirmation that there is no atomic-scale interdiffusion in our samples at room temperature. As a further check, we have annealed a sample covered with 1 ML of Au for 5 min at 175 and 240°C to induce interdiffusion. The Au 4f signal was found to decrease and the binding-energy shift became +0.1 eV, as expected for alloy formation.

Next we consider whether reconstruction can account for the fact that the shift in the Au monolayer on Ag is much smaller than that in the first atomic layer on Au itself. By lowering the energy of the system, reconstruction of the Au(111) surface will increase the core-electron binding energy, making the surface shift less negative. For Au on Ag(111) there is no evidence of reconstruction. The effects of reconstruction are therefore also opposite to those observed, and cannot be dominant in this system.

Finally, we examine the connection between the core-electron shift and the *d*-band width, established in the study of the first atomic layer of bulk gold.⁵ The surface-atom core-level shift of Au was shown to be due to the narrowing of the Au 5*d* band at the surface, and

the concomitant flow of charge from delocalized 6*s* states into more localized 5*d* states, while maintaining layerwise charge neutrality.¹⁷ The core-electron binding-energy shift in the Au monolayer on Ag(111) is, however, only half as large¹⁴ as that of the first atomic layer of the Au(111) surface,⁶ while the Au 5*d* band of the monolayer on Ag is much narrower than that of the first layer on Au. The greater *d*-band narrowing would lead us to expect an even greater, negative 4*f* shift for Au on Ag(111). The magnitude of the core-electron binding-energy shift of the Au monolayer is consequently not interpretable solely in terms of the narrowing of the band structure of the monolayer. Band narrowing is, however, only one of a number of mechanisms that affect the core-electron binding energies of an adsorbed monolayer. Another that is likely to be important is charge transfer, but the experiment offers no independent measure of its contribution.

For a quantitative interpretation of the shifts of the monolayers we turn to the Born-Haber formalism, first considering the isolated adsorbed atom and then progressing to the adsorbed monolayer. The cycle illustrated in Fig. 4 is similar to that used by Johansson and Mårtensson¹ to relate the core-electron binding energy in a metal to that of its free atoms with atomic number *Z*. The cycle contains the first ionization potential of the atom with next-higher atomic number, the cohesive energies of the *Z* and *Z* + 1 metals, and an implantation term. In the present case the cohesive energies are replaced by adsorption enthalpies, and the implantation term vanishes. The cycle starts with the adsorbed atom on a substrate. In the first step it is desorbed. The resulting free atom is photoionized, and replaced by its valence-ionized *Z* + 1 atom. This atom is neutralized and reabsorbed on the surface. The result is equivalent to a core-ionized, fully-screened adsorbate atom of the original kind, and the energy required to traverse the cycle is equal to the core-electron binding energy, measured relative to the Fermi level of the substrate:

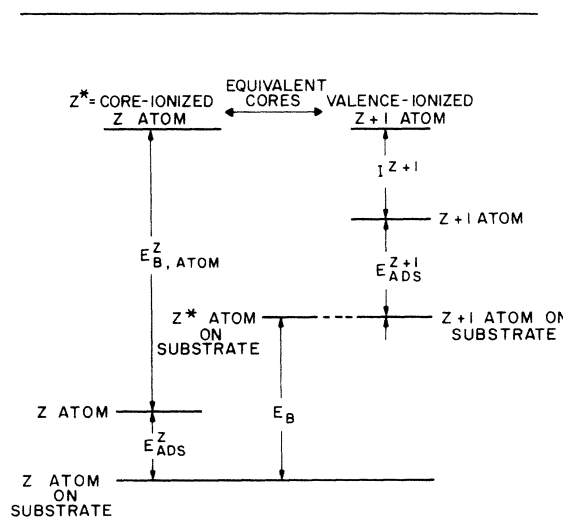


FIG. 4. Born-Haber cycle relating the core-electron binding energy of an adsorbed, isolated atom with atomic number *Z* to the adsorption enthalpies of the *Z* and *Z* + 1 atoms.

$$E_B^{\text{ads}} = E_B^{\text{atom}} - I^{Z+1} + E_{\text{ads}}^Z - E_{\text{ads}}^{Z+1}. \quad (1)$$

A correction to this formulation is needed if the $Z+1$ atom has an atomic radius greatly different from that of the original adsorbate atom. Under those circumstances the final-state atom created by core ionization does not lie at its equilibrium distance from the surface, and therefore may have significant vibrational energy. In the cases considered here this effect will be small because the atomic sizes of Au and Hg differ by only 0.03 Å.

For numerical evaluation we use the free-atom core-electron binding energy for $\text{Au}_{7/2}$ of Johansson and Mårtensson, 91.52 eV, and the known 10.44-eV ionization potential of Hg. These, together with the cohesive energies and the implantation term, give a value for the Au $4f_{7/2}$ core-electron binding energy in the bulk metal very close to the experimental one of 84.0 eV. For the case of the isolated adsorbed atom, the adsorption enthalpies are taken from the work of Miedema and Dorleijn.³ The resulting core-electron binding energies for the isolated Au adsorbate atom on Ag, Au, and Pt are 83.05, 82.95, and 82.74 eV, or expressed as shifts relative to the bulk value, -0.95, -1.05, and -1.26 eV; see Table I. These shifts are much larger than those measured for atoms in the corresponding adsorbed monolayers, -0.17, -0.35, and -0.40 eV, indicating the importance of the in-plane cohesive interactions within the adsorbed layer.

We next construct a Born-Haber cycle appropriate for an adsorbed monolayer by introducing the cohesive interactions within the adlayer, E_{agr} , as well as the implantation term representing the transfer of a $Z+1$ atom from an island of adsorbed $Z+1$ atoms to the original island of Z atoms; see Fig. 5. This cycle yields the following relationship:

$$E_B^{\text{ML}} = E_B^{\text{atom}} - I^{Z+1} + E_{\text{agr}}^Z + E_{\text{ads}}^Z - E_{\text{agr}}^{Z+1} - E_{\text{ads}}^{Z+1} - E_{\text{impl}}. \quad (2)$$

Comparing Eqs. (1) and (2), we find that the difference between the binding energies in the isolated atom and the monolayer lies in the difference between the monolayer aggregation energies, and the implantation term:

$$\Delta E_B = E_{\text{agr}}^Z - E_{\text{agr}}^{Z+1} - E_{\text{impl}}. \quad (3)$$

Based on the results for the bulk case,¹ it seems likely that the implantation term can be neglected. Applying this equation to a gold adsorbate layer, it is clear that the major contribution to ΔE_B should come from the cohesive energy of the gold layer in the initial state. The last

TABLE I. Core-electron binding-energy shifts in eV for Au atoms on metallic substrates.

Substrate	Monolayer (Expt.)	Isolated atom (Born-Haber)	ΔE_{agr}
Ag(111)	-0.17 ^a	-0.95	0.78
Au(111)	-0.35 ^b	-1.05	0.70
Pt(111)	-0.40 ^c	-1.26	0.86

^aSee Ref. 14.

^bSee Ref. 6.

^cSee Ref. 7.

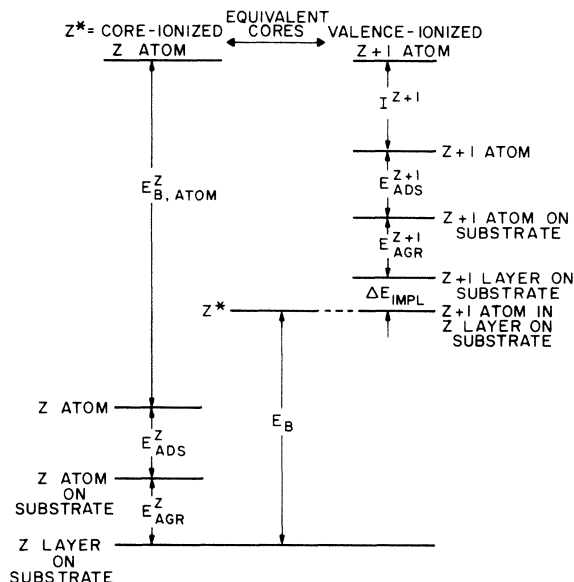


FIG. 5. Born-Haber cycle for atoms in an adsorbed monolayer.

column in Table I shows the values for ΔE_{agr} , taken to be equal to ΔE_B and derived from the measured monolayer shift and the calculated adsorbate atom shift.

In view of the 3.8% difference between the lattice constants of Au or Ag and Pt, it is surprising that ΔE_{agr} is so similar on all three substrates. The core-electron binding-energy shift for Au on Pt(111) is indeed more negative than that of the first monolayer of Au(111), as one might expect on the basis of an increase in the conduction electron density due to a compression resulting from the smaller Pt lattice constant, but the effect is small, only 0.05 eV. This can be understood in terms of the observation¹⁸ that the first monolayer on Au(111) itself undergoes a 4.6% uniaxial contraction due to the increased localization of the outer electrons. The residual discommensuration strain for Au on Pt is probably relieved by dislocations, minimizing the effect on the monolayer cohesive energy. At moderate coverage this strain can be relieved by breaking the adsorbate up into small islands. Evidence for such a breakup is found in the rapid transition to a much larger negative surface-atom shift as the coverage is reduced well below 1 ML.⁷ A shift of -1.0 eV, found in the limit of low coverage, was attributed to the edge atoms of monolayer islands.⁷ This value is not much smaller than that calculated above for the isolated adsorbate atom, and is therefore appropriate for very small clusters with limited in-plane cohesive interactions, or, equivalently, islands that consist almost entirely of edge atoms.

The average value for the monolayer aggregation energy, ~ 75 KJ/mole, is very much smaller than the adsorption enthalpies, 275, 295, and 360 KJ/mole for Au on Ag, Au, and Pt, respectively. An examination of the data in Ref. 3 shows that for many substrates the atomic adsorption enthalpy of a given metal is a comparable to its cohesive energy. The cohesive interaction within the monolayer is then likely to be small. Under those cir-

cumstances, as the temperature is raised islands will break up into isolated atoms long before the atoms desorb from the surface. As a result, desorption enthalpies obtained from dynamic desorption measurements typically refer to the isolated atom, even when the coverage is a reasonable fraction of a monolayer. (This is also implicit in the good agreement between measured and empirical isolated-atom adsorption enthalpies noted in Ref. 3.) Photoemission experiments, on the other hand, typically yield information for atoms in island, layers, or clusters. Experiments on isolated adsorbate atoms require evaporation onto substrates sufficiently cold to suppress diffusive motion, which normally causes atoms to be trapped by steps and defects, even at extremely low coverage.

CONCLUSIONS

Experimental core-electron binding-energy shifts for atoms in adsorbed monolayers are used, in conjunction

with values calculated from a Born-Haber cycle for adsorbed isolated atoms, to obtain the cohesive energy within the adsorbed monolayer. For Au on a variety of substrates this aggregation energy is ~ 75 KJ/mole. The $5d$ -band structure of a Au monolayer on Ag(111) is found to be narrowed relative to that of bulk gold by an amount somewhat less than predicted on the basis of the change in Au coordination number. The binding-energy shift of the Ag $3d$'s at higher coverage can be understood in terms of the bending of the band at the interface between two metals with different work functions.

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