PHYSICAL REVIEW B VOLUME 34, NUMBER 10 15 NOVEMBER 1986

Properties of epitaxial Au on W(100)

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(Received 10 October 1985)

For coverages less than 1 monolayer, Au grows epitaxially on W(100); above that coverage it forms misoriented islands or crystals with bulk properties. The *d* band of the Au monolayer indicates that there is appreciable overlap between the 5*d* wave functions of the adsorbate layer, even though the distance between Au atoms is 10% greater than in the metal. The core-electron binding energy of the gold monolayer is 1 eV larger than that calculated from adsorption enthalpies for the isolated gold atom, indicating that the cohesive interactions within the monolayer are comparable to those in bulk gold.

I. INTRODUCTION

A Born-Haber cycle analysis[1] has demonstrated a close connection between the cohesive energy of a metal, E_{coh}, and the core-electron binding energy of its atoms, E_B. The cycle yields the following relationship:

$$E_B = E_B^{\text{free}} - I^{Z+1} + E_{\text{coh}} - E_{\text{coh}}^{Z+1} - E_{\text{impl}} \ ,$$

where E_B^{free} is the core-electron ionization potential of the free atom, I^{Z+1} is the ionization potential of the element with next-larger atomic number, E_{coh}^{Z+1} its cohesive energy, and E_{impl} the energy required to move one atom from a metal of $Z+1$ atoms into one of Z atoms. Of these terms the first two are atomic properties, independent of the binding of the atom in the solid, and the last one has been shown to be small compared to the cohesive energies. The major solid-state perturbation of the core-electron binding energy then comes from the two cohesive energies. This analysis has been extended to calculate the core-electron binding-energy shift of surface atoms by introducing the surface cohesive energy.[1,2] It has also been shown that for adsorbate atoms the adsorption enthalpies replace the cohesive energies.[3,4] This makes it possible to obtain more details about the energetics of metal-on-metal heteroepitaxy than is available from desorption studies.

We have examined the growth of fcc Au on the (100) surface of bcc W using low-energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS) in order to study the interaction of the Au atoms with the substrate and with each other. This is a particularly favorable system since Au is insoluble in W and does not form intermetallic compounds with it. The desorption of Au from the W(100) surface has been previously studied[5] and is not reexamined here, especially since an empirical estimate of the adsorption enthalpies[6] yields results in excellent agreement with experiment. The growth of Au on W(100) has also been thoroughly explored.[7]

II. EXPERIMENTAL DETAILS

The overlayer systems were prepared by depositing Au atoms from a Knudsen cell onto clean W(100) surfaces in a preparation chamber operating in the 10^{-10}-Torr range. The chamber is attached to a Hewlett-Packard HP-5950A ESCA (electron spectroscopy for chemical analysis) spectrometer, utilizing monochromatized Al $K\alpha$ radiation, so that the samples can be moved into the measurement region without exposure to higher pressure. The W single crystal was initially cleaned by argon-ion sputtering, but most of the subsequent surface preparation consisted of electron-bombardment heating to temperatures approaching 200 °C. Carbon contamination was removed by heating in an atmosphere containing oxygen. The resulting oxide was removed by heating in vacuum. The surface conditions were checked by LEED and XPS, the latter indicating that both oxygen and carbon could be reduced to a few percent of a monolayer (ML). Freshly cleaned surfaces showed a growth of oxygen contamination with high sticking coefficient. Gold-covered surfaces remained free of contamination during the 30—60 min required to obtain the Au 4*f* data, but showed a modest growth of both oxygen and carbon during the 10 h required for the valence-band data. Both the gold and the contamination were readily removed by heating to 1750 °C.

The gold-deposition furnace was typically operated at 700 °C and stabilized to within 1°. The deposition rate was calibrated with a quartz-crystal microbalance. The gold was deposited immediately after flashing the crystal in vacuum, while it was still hot, to allow the adsorbate atoms to reach equilibrium lattice sites. The vacuum during the deposition was in the 10^{-9}-Torr range. The amount of gold actually deposited on the sample was determined from the gold-induced attenuation of the W 4*f* signal of the substrate, as well as in terms of the strength of the gold 4*f* signal itself. Both methods require a reliable value for the electron mean free path in gold at ~1400 eV. We used the well-documented value of 19 Å obtained for polycrystalline gold.[8] The gold coverages calculated from the deposition rate and time and those obtained from the core-electron signal strengths were generally in agreement to better than 10%. The point of monolayer coverage, determined from the break in the slope of a plot of the Au 4*f* signal against coverage, corresponded to a coverage of 1×10^{15} atoms/cm^2.

III. RESULTS

A. LEED observations

A freshly cleaned W(100) surface produces a fuzzy centered $(\sqrt{2}\times\sqrt{2})R45°$ pattern[9-11] like that shown in Fig. 5(a) of Ref. 11. Hydrogen adsorption became evident within 30 min. At Au coverages close to 1 ML a $p(1\times1)$ LEED pattern is obtained, indicating that the gold forms an ordered overlayer and prevents the reconstruction of the W(100) surface. This pattern is stable for extended periods, indicating that hydrogen adsorption is reduced by the Au overlayer. For coverages beyond 1 ML, the LEED pattern becomes progressively weaker, and vanishes after 3 or 4 ML have been deposited. This is in accord with Ref. 7, where it is shown that only the first ML grows epitaxially on the W(100) surface. Additional gold results in the growth of gold with bulklike properties, initially as an incommensurate, compressed layer with 1.5×10^{15} atoms/cm^2, and then as misoriented, three-dimensional gold crystals.

B. Core-electron spectra

For coverages less than 1 ML the Au 4*f* lines have a largely coverage-independent binding energy and a width 0.2 eV greater than that of the bulk metal, see Fig. 1(a). This suggests that in this coverage regime the gold occupies a unique site, i.e., the local environment of the gold atoms remains unchanged. The excess width may be due to increased vibrational broadening, which has frequently been reported for surface atoms. The binding energy is 0.31 eV greater than that in bulk Au. When the coverage exceeds 1 ML, a new line at a binding energy somewhat smaller than that of bulk gold appears, and grows in intensity as the coverage is increased. (The binding energy was model dependent, and could not be determined with high accuracy by least-squares analysis.) The new line is associated with the incommensurate, compressed gold layer mentioned above. At higher coverage the gold 4*f* line moves to the bulk value appropriate for the misoriented, three-dimensional crystals, Fig. 1(c).

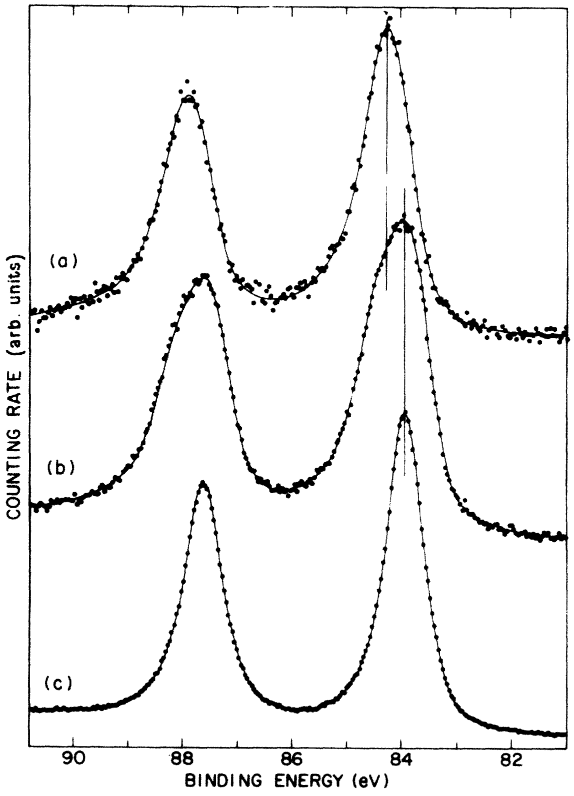

FIG. 1. Gold 4*f* spectra for various coverages of Au on W(100). (a) 0.8 ML. (b) 2.4 ML. (c) Thick Au layer.

C. Valence-band spectra

The valence band of clean tungsten, shown in Fig. 2(a), is in good agreement with the density of states calculated

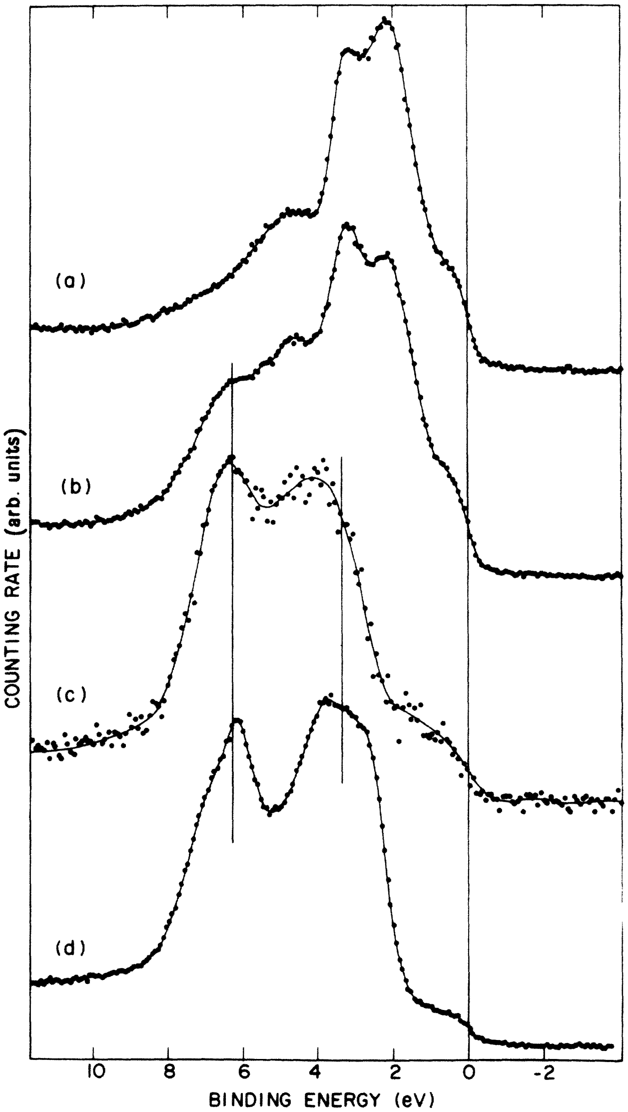

FIG. 2. Valence-band spectra of tungsten and gold. (a) The clean W(100) surface. (b) W(100) covered with 1.0 ML of Au. (c) The Au-induced component of (b). (d) Polycrystalline Au.

by Mattheiss,[12] which has peaks 1.8, 3.3, and 4.7 eV below the Fermi level. The data are not particularly sensitive to surface contamination and should provide a reasonably good image of the bulk density of states, since only ~20% of the W 5*d* signal comes from the surface atoms. XPS is consequently not a sensitive method for the study of the modification of the surface band structure by an overlayer, but an ultraviolet photoemission spectroscopy (UPS) study of the effects of Au on the surface states of W(100) has recently been reported.[13] XPS should be more suitable for a study of the Au adsorbate layer, since the Au 5*d* cross section[14] is four times as large as that of W 5*d*. The strong signal produced by 1 ML of gold in Fig. 2(b) confirms this supposition. The gold-induced signal can be isolated by subtracting the W contribution, provided the tungsten spectrum is not significantly modified by the Au overlayer. Considering the 0.55-eV resolution of our spectrometer, and the fact that 80% of the W 5*d* signal comes from atoms in the bulk, this is not an unreasonable assumption. For the subtraction we use the valence band of the clean surface, attenuated by the same amount as the corresponding W 4*f* core-electron spectrum. This subtraction procedure,[8] which then has no adjustable parameters, leads to the result shown in Fig. 2(c). The difference spectrum has no peaks or negative excursions in the region of the W 5*d* spectrum, indicating that there are no significant overlayer-induced changes in the W valence band within the resolution of the XPS data. The result should therefore be a reasonable representation of the Au 5*d* band of the overlayer. The width of the band at half height is 4.49 eV, that of the *d* band of bulk gold, shown below for comparison, is 5.17 eV. This narrowing of 13% is substantially greater than that of 8% found for the *d* band of the first monolayer on bulk gold.[8] The narrowing is accompanied by centroid shift of 0.29 eV.

IV. DISCUSSION

A. Growth mechanism

Both the LEED and XPS data confirm that the first monolayer of gold grows epitaxially on the W(100) substrate.[7] This is in accord with expectations, since the adsorption enthalpy of Au on W(100) (Refs. 5 and 6) is greater than the cohesive energy of Au. The fact that the core-electron binding energy does not vary appreciably in this range indicates either that the lateral interactions between gold atoms are very small, or that the gold forms large, two-dimensional islands in which all but the peripheral atoms have identical environments. The 4.49-eV width of the Au 5*d* band of the monolayer, compared to that in CsAu in which the gold atoms are well separated and have an atomiclike 5*d* spectrum with 1.5-eV spin-orbit splitting,[15] favors the latter interpretation. Island structure, with interior and peripheral atoms, may also contribute to the excess width of the 4*f* electron spectra in this regime. We shall see below that the magnitude of the Au 4*f* core-electron binding energy also requires large cohesive interactions within the monolayer.

For coverages beyond 1 ML the weakening of the $p(1\times1)$ LEED pattern indicates that even the second layer fails to grow epitaxially. This is not surprising since the separation between the atoms in the first monolayer is 10% greater than that in metallic gold; undoubtedly too large to allow growth of a strained fcc lattice.[16] The incommensurate layer which does grow is already largely bulklike.[7] The small negative shift of the core-electron binding energy in this phase can be understood in terms of the negative surface-atom shift of bulk Au.[8] For the (111) and (100) surfaces of Au, the surface-atom core-level shifts are 0.35 and 0.38 eV.[17] Shifts close to the (111) value have also been obtained for second atomic layer of Au on Ag(111),[18] indicating that the shift does not require a bulk Au substrate. A thin Au multilayer should consequently have a core-electron binding energy which reflects the average of its bulklike interior and modified surface atoms, explaining the observed small negative shift.

The growth of gold in misoriented three-dimensional crystals is confirmed by data taken at high coverage. Here the 4*f* signal from the tungsten substrate remains visible even after Au amounting to many times the escape depth has been deposited. Au on W(100) clearly does not exhibit layerwise growth, and conforms to the Stranski-Krastanov mechanism.

B. Comparison with the adsorption enthalpy

The core-electron binding energy of the *isolated* Au adsorbate atom E_B^{ads} can be obtained from the known adsorption enthalpies E_{ads} of Au and Hg on tungsten, using a Born-Haber cycle[3,4] yielding the relationship:

$$E_B^{\text{ads}}=E_B^{\text{free}}-I^{\text{Hg}}+E_{\text{ads}}^{\text{Au}}-E_{\text{ads}}^{\text{Hg}} .$$

The Au $4f_{7/2}$ electron ionization potential of the free Au atom is 91.52 eV relative to the vacuum level.[1] The first ionization potential of Hg is 10.44 eV. The adsorption enthalpy of Au on W(100) for small coverage is 4.13 eV according to Bauer *et al.*[5] This value, obtained for coverages below $\frac{1}{2}$ ML and a frequency factor of 10^{13} sec^{-1}, is in good agreement with the semiempirical estimate of Miedema and Dorleijn[6] for the isolated adsorbate atom. Alternate values for the enthalpy, obtained in Ref. 5 by allowing the frequency factor to vary, decrease from 5.8 to 3.4 eV in the range from 0 to 1 ML. According to the above equation, this implies a corresponding shift in core-electron binding energy. Experimentally we find no such change in this range of coverage. We conclude that the strong modulation of the enthalpy is an artifact arising from the large (7 orders of magnitude) change of the frequency factor, and reject the results of this analysis. The adsorption enthalpy for Hg is 1.92 eV according to Swanson *et al.*[19] Inserting these values into the above equation yields a $4f_{7/2}$ electron binding energy of 83.3 eV for the isolated Au adsorbate atom on a W(100) surface.

This value is 1 eV smaller than that obtained experimentally for gold coverages in the monolayer range on W(100). The difference between the binding energy computed for the isolated atom and that measured for finite coverage has its origin in the in-plane interaction between the adsorbate atoms.[4] The large width of the Au 5*d* band of the adsorbate layer compared to the atomiclike 5*d* spectrum of CsAu (Ref. 15) already gave an indication

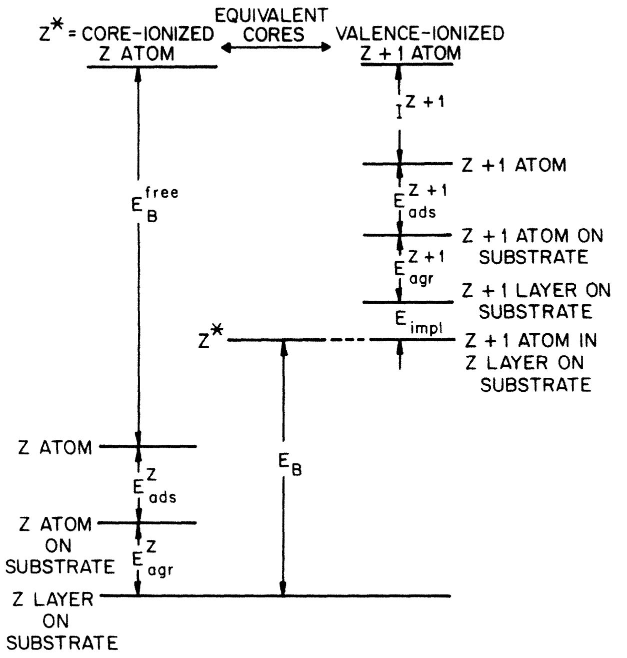

FIG. 3. Born-Haber cycle for a monolayer adsorbate on a metal.

that this interaction is strong. A Born-Haber cycle which includes the interaction between adsorbate atoms contains three additional terms, the in-plane cohesive interaction within the Au adsorbate layer $E^{\rm Au}_{\rm agr}$, the corresponding interaction within a Hg layer, and the energy $E_{\rm impl}$ required to move a Hg atom from the Hg layer into the Au layer, see Fig. 3. The binding-energy shift ΔE due to the aggregation of isolated adsorbate atoms into a monolayer is given by

$$\Delta E = E^{\rm Au}_{\rm agr} - E^{\rm Hg}_{\rm agr} - E_{\rm impl}\ .$$

The value for ΔE is 1.0 eV according to the above discussion. Based on the magnitude of implantation energies for solids, the last term can probably be neglected. The scale for the other terms is set by the cohesive energies of Au and Hg, which are 3.81 and 0.62 eV, respectively. The in-plane interaction will consequently be dominated by the contribution of the Au adsorbate layer, which will make a positive contribution to ΔE. Since a Au atom on the (100) surface has four gold neighbors, a simple scaling of the cohesive energies by the coordination number yields a shift of 1.1 eV. A similar argument was successfully used to estimate the core-electron binding-energy shift for the first atomic layer of bulk metals,[1] suggesting that the agreement may not be fortuitous. However, considering the 10% greater distance between Au atoms, it seems likely that the Au-Au interaction takes place via the substrate.

C. Electronic properties of the adsorbate layer

The positive (0.31 ± 0.04)-eV core-electron shift of the adsorbed monolayer is equal within the experimental uncertainty to the (0.29 ± 0.1)-eV centroid shift of the $5d$ band. This agreement is in accord with the predicted and observed behavior of the first monolayer of bulk gold.[8] The sign of the shift in that latter case is, however, opposite to that found here, even though the $5d$ band of the monolayer shows valence-band narrowing, corresponding to an even greater reduction in s-d hybridization. The difference between the two cases may lie in differences in orbital occupancy in the initial state, or else in a difference in core hole screening in the final state. In the case of bulk gold the surface layer remains neutral, and screening within the surface layer is comparable to that in the bulk.[8,20] When two dissimilar metals are in contact both constraints are relaxed. Since Au has a slightly larger electronegativity than W, charge transfer is not likely to increase the binding energy. However, the large adsorption enthalpy of Au on W(100) requires hybridization between Au and W orbitals which may be responsible for positive shift. This points to a direct connection between a specific term in the Born-Haber cycle and the observed shift. Another positive contribution may arise from the less efficient screening of the core hole by the two-dimensional s-band of the adsorbed Au monolayer. It will be interesting to test these suppositions in other overlayer systems.

D. Comparison with shifts in metal clusters

Positive Au $4f$ core-electron binding-energy shifts, comparable in magnitude to the shift found here below 1 ML, have also been reported for Au clusters grown on amorphous carbon.[21–23] In these clusters the dominant cohesive interactions are between the atoms of the cluster itself, and the shift arises from the self-energy of the charged cluster in the final state. Small monolayer islands, which are strongly coupled to a metal substrate, are entirely different entities in which the shift has an electronic origin. Their core-electron binding-energy shifts are well accounted for by the Born-Haber approach used here. The inherent distinction between these two types of systems is obscured when the term "cluster" is applied to both.

V. CONCLUSIONS

The first monolayer of Au deposited on W(100) grows epitaxially and inhibits surface reconstruction. Further deposition leads to the growth of unoriented gold layers and crystals. The lateral interaction within the monolayer results in the formation of Au $5d$ band with appreciable width, and significantly increases the core-electron binding energy beyond that of the isolated adsorbate atom.

ACKNOWLEDGMENT

We are indebted to P. H. Citrin for comments on the manuscript.

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