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Electronic structure of Au and Ag overlayers on Ru(001): The behavior of the noble-metal *d* bands

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The metal *d* bands of Au and Ag individually adsorbed on Ru(001) have been observed with photoemission as have the core 4*f* levels of Au. The adlayer *d* bands display shifts in their centroids as well as band narrowing due to having fewer noble-metal nearest neighbors relative to bulk metals. The narrowing may be monitored by measuring the doublet nature of these valence-band densities of states or by sampling the overall *d*-band width with the former not susceptible to instrumental broadening problems. These widths receive contributions from spin-orbit splitting $\Delta_{\text{s.o.}}$ and intrinsic *d*-band effects Δ_{band}. These have been separated and the inferred Δ_{band} for a Au monolayer suggests that the substrate is contributing measurably to the Au bandwidth while having little or no effect on Ag. Providing that the Au adlayer 4*f*-level shifts are measured with respect to the surface of Au rather than the bulk, a consistent picture of *d*-band and core-level chemical shifts emerges that, granted the lower number of unlike nearest-neighbor atoms, is compatible with what has been previously observed for bulk noble-metal alloys.

I. INTRODUCTION

The electronic structure of materials with unusual dimensions (clusters, nanostructures, and overlayers) has recently attracted much attention in a wide variety of systems in connection with the search for new materials. Noble-metal overlayers and their alloys on a well-defined substrate are prototype systems that have been intensely studied.[1–9] Some of the fundamental issues are the growth mode of the overlayers on a substrate, the change in electronic structures as a function of coverage, the nature of the interfacial interaction, and whether or not two-dimensional alloying occurs at any coverage on the substrate surface when two or more metals are codeposited.

The objective of this work is to investigate the electronic structure of two systems: Au and Ag deposited individually on a Ru(001) substrate at room temperature from the submonolayer region (0.4 ML) to the multilayer region (3 ML). High-resolution photoemission spectroscopy with synchrotron radiation together with thermal desorption were used in the investigation. Emphasis is placed on the behavior of the noble-metal *d* bands as a function of coverage.

Au and Ag are prototype noble metals with fcc structure and nominally filled *d* bands, which display significant relativistic effects (both *d* bands exhibit an unmistakable spin-orbit-splitting signature). Neither Au nor Ag form bulk alloys with Ru and neither diffuses into the Ru(001) substrate. The growth mode of Au and Ag on Ru(001) is known to be pseudomorphic with Ru(001), which is identical to fcc(111) in packing, and follows a Stranski-Krastanov growth mechanism; although, in the case of Ag, the first layer does not appear to be filled until the coverage reaches ~1.5 ML.[7,10] The Au and Ag layers are significantly compressed within the layers in the pseudomorphic regime since both Au and Ag have larger metallic radii than does Ru. At submonolayer coverage, Au forms dendrite-type two-dimensional islands instead of isolated Au atoms;[11] Ag is expected to exhibit the same behavior. The lower surface energies of Au and Ag compared to Ru make it energetically favorable for them to cover the Ru substrate despite the tendency not to alloy with Ru since surface-energy factors modify bulk bonding trends.

Photoemission was used in this study because both the Au and Ag *d*-band densities of states are very sensitive to this technique. Small changes in the electronic structure can often be revealed by photoemission measurements of the valence band,[12,13] especially when synchrotron radiation (tunable) is used as the light source. It has been known for some time that the Au-Au *d*-*d* interaction in bulk Au is very strong; any attempt to reduce this direct interaction, such as alloying, will reduce the intrinsic Au *d*-band bandwidth and the associated apparent spin-orbit doublet splitting[12,13] and tends to push the centroid of the Au *d*-band component away from the Fermi level. This trend is often accompanied by a Au 4*f*-level shift away from the Fermi level. In this study, the change in electronic structure of the noble-metal overlayers on Ru(001) at coverages from submonolayer to multilayer were closely monitored with photoemission. Thermal desorption was used to monitor the dosing rate and the coverage. In the following, binding-energy shifts, which are particularly relevant to the interpretation of our results, are discussed in Sec. II. Experimental procedures are given in

Sec. III, followed by results in Sec. IV, and analysis and discussion in Sec. V.

II. BINDING-ENERGY SHIFTS

As noted above, both Ag and Au display well-defined *d*-band doublets as well as core-levels binding-energy shifts upon alloying. The doublet splitting, however, arises from a combination of spin-orbit splitting and *d*-band broadening effects, with the latter causing a doubling of the doublet-peak splitting (~2.7 eV) over that characteristic of free-atom spin-orbit splitting (1.52 eV). These combined effects can be described crudely in terms of an apparent spin-orbit splitting of the form[14]

$$\Delta = \sqrt{\Delta^2_{\text{s.o.}} + \Delta^2_{\text{band}}}\,,$$

where $\Delta_{\text{s.o.}}$ is the true atomic spin-orbit splitting and Δ_{band} the band-broadening contribution. The rather localized *d* charge and the core levels have different radial distributions and sample the chemical changes in the potential differently, thus giving different contributions to the binding-energy shifts. The *d* bands are also directly involved in bonding with the other alloy constituent. There is such bonding between the Ru substrate atoms and the noble-metal adatoms although, on average, it is weaker than the bonding between like atoms. The bulk of the other constituent's valence-electron levels lie above the occupied *d* bands of Au and Ag. Hybridization of that valence-electron character into these noble-metal *d* bands causes them to be depressed resulting in a chemical shift in the direction of increased binding.

In the case of Au alloying, it has been observed[3] that due to hybridization into the occupied Au *d* bands by the other alloy constituent, there is a depletion in *d* count, a deepening of the potential in Au site and, in turn, increased binding in the Au. Whether or not the increased binding is indicative of charge loss at the Au site depends on the extent to which the non-*d* charge screens the *d* depletion and on the bonding associated with that charge. Very likely, the net charge transfer is consistent with Pauling's view that Au is the most electronegative of the metallic elements, and the sign of the Au binding-energy shifts is contrary to the actual charge transfer.

There are yet other contributions to changes in the potential; for example, there are extra atomic "Madelung" terms coming from any net charge outside the sampling atomic charge. There are also "bonding-antibonding" charge-redistribution contributions to a binding-energy shift. A *d*-wave function near the bottom of the *d* band is flat at the midpoint between atoms, while the one near the top of the *d* band is noded; this wave-function character changes continuously across the band. This trend from flat (bonding) to noded (antibonding) is attended by a measurable contraction of a *d* electron's charge and, thus, an increase in the electron's contribution to the local potential. Calculations[15] suggest that this can be a significant source of changing electron-energy levels on going from a bulk alloy to a surface adatom. The latter is involved with bonding with fewer near neighbors and the relative number of like versus unlike neighboring atoms changes. This affects the balance of bonding-antibonding character in the local valence charge. Despite all of the above-mentioned complications, the experimental results to be reported here appear to have a plausible chemical explanation.

III. EXPERIMENTAL

Photoemission experiments were carried out at the grasshopper beamline of the Canadian Synchrotron Radiation Facility at Synchrotron Radiation Center (Aladdin), University of Wisconsin-Madison. An 1800-gr/mm grating was used to achieve a photon resolution of ~0.2 eV at 70 eV. Noble-metal overlayers were prepared *in situ* in a UHV chamber (base pressure of 2×10^{-10} Torr) by depositing onto a clean Ru(001) substrate from resistively heated dosers at a rate of ~1 ML/min as calibrated with a UTI-100 quadrupole mass spectrometer and thermal desorption.

The valence-band spectra of Au and Ag overlayers were recorded at 70-eV photon energy with a Leybold hemispherical electron-energy analyzer operating in an angle-integrated mode with a 25-eV pass energy. All data are normalized to the incoming photon flux monitored with a Ni metal mesh located in the vicinity of the exit slit of the monochromator. Corresponding Au 4*f* binding-energy shifts were also recorded for some of the systems at 170-eV photon energy at a resolution of ~0.3 eV.

IV. RESULTS

Figure 1 shows the coverage-dependant valence-band spectra of Au/Ru(001) recorded at room temperature with 70-eV photon energy. The spectrum of the clean substrate is also shown for comparison. Similar series of spectra are shown for Ag/Ru(001) in Fig. 2, together

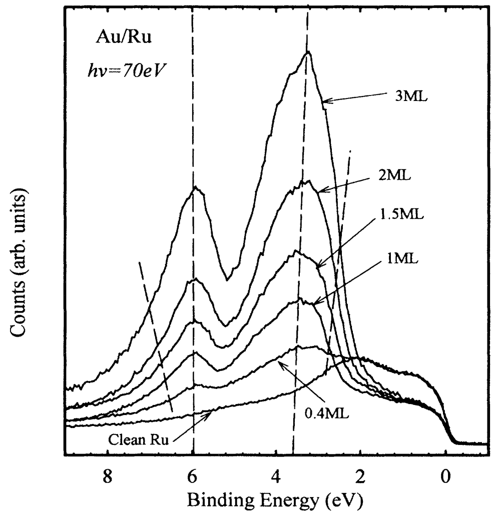

FIG. 1. Photoemission spectra taken at photon energy of 70 eV as a function of coverage of Au on Ru(001). The broken line connects the *d*-band edges as well as the apparent spin-orbit-splitting maxima.

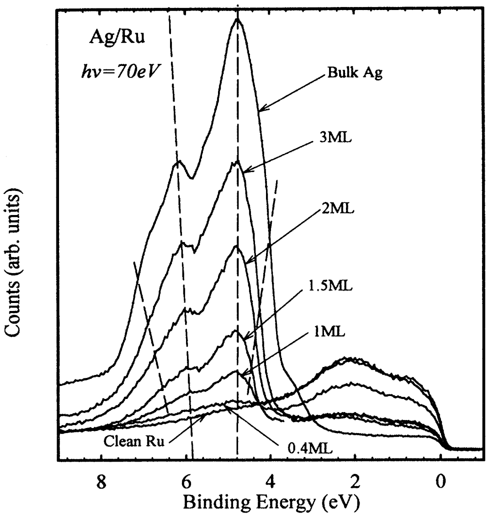

FIG. 2. Photoemission spectra taken at photon energy of 70 eV as a function of coverage of Ag on Ru(001) and bulk Ag. The broken line connects the *d*-band edges as well as the apparent spin-orbit-splitting maxima.

with that of a bulk Ag sample. When making comparison between the figures, it should be remembered that the transition probabilities are stronger for Au than they are for Ag and Ru at the photon energy used. Several features common to both sets of data are immediately apparent. First, the intensities of the noble-metal *d* bands as well as the bandwidths and apparent spin-orbit doublet splittings increase as the coverage increases from submonolayer (0.4 ML) to multilayer (3 ML). The spectrum for 3 ML of Au on Ru(001) already exhibits the bulk appearance, as far as the splitting is concerned, while the spectrum for the 3 ML of Ag on Ru(001) is approaching that of the bulk Ag. Second, the substrate signal is quenched almost entirely when 1-ML coverage of Au and 1.5 ML of Ag are reached. This is consistent with the short escape depth of the low-kinetic-energy electrons (~ 60 eV) and can be used to infer that the Ru substrate is entirely covered at the corresponding coverages. This is consistent with previous findings.[6,7] It is to be expected that it takes more Ag than Au to completely cover the substrate because Ag shows less of a tendency for bulk alloying with transition elements such as Ru and because its desorption energy (from Ru) is less than that of Au.[16] In Au(Ag), the lower peak is largely of $5(4)d_{3/2}$ character while the upper is primarily $5(4)d_{5/2}$. What at first glance is a surprising result is the movement of the noble-metal *d*-band peaks. For Au on Ru(001), the Au "$5d_{3/2}$" component remains stationary at ~ 6 eV below the Fermi level while the Au "$5d_{5/2}$" component moves towards the Fermi level from 3.6 to 3.3 eV as the coverage increases from 0.4 to 3 ML; but, in the case of Ag, the Ag "$4d_{5/2}$" component is the one that is stationary (~ 4.8 eV), while the Ag "$4d_{3/2}$" component moves away from the Fermi level (5.7–6.0 eV) as the coverage increases from 0.4 ML to the bulk value. This separate behavior arises from an interplay of the variation of peak splittings and overall shifts in the bands. If one takes the Ru spectrum and suitably normalizes it so as to make a background subtraction for an adlayer spectrum, one finds that the resulting centroids of the metal *d* bands move toward the Fermi level with increasing coverage for both Ag and Au, as will be seen in the next section.

The Au core-level $4f$ spectra of 0.4, 1, 1.5, and 3 ML Au/Ru(001) have also been obtained.[17] While the 0.4, 1, and 1.5 ML spectra exhibit one Au $4f_{7/2}$ peak, the 3-ML spectrum exhibits a distinct shoulder at the higher binding-energy side. A two-peak fit to the 3-ML data shows a Au $4f_{7/2}$ peak at a binding energy of 83.99 eV, similar to that of the bulk Au, and another peak at 83.64 eV, characteristic of the surface atom of bulk Au.[18] The $4f_{7/2}$ peak for the 1 ML Au lies between these two binding energies at 83.88 eV and increases in binding energy by 0.05 eV for the 0.4-ML coverage. The trend reverses on going above 1-ML coverage; this can be understood as arising from an increasing bulklike Au component in the peak. This result is consistent with previous low-resolution measurements.[16] Due to a low-instrument resolution at the energies involved, it was not practical to obtain Ag (or Ru) $3d$ core-level results in this experiment. However, x-ray photoemission spectroscopy (XPS) measurements[7,19] have shown the same trend for Ag as is observed here for Au.

V. ANALYSIS AND DISCUSSION

A. General considerations

To facilitate the discussion, we have plotted in Figs. 3–5 some of the parameters of interest, which can be de-

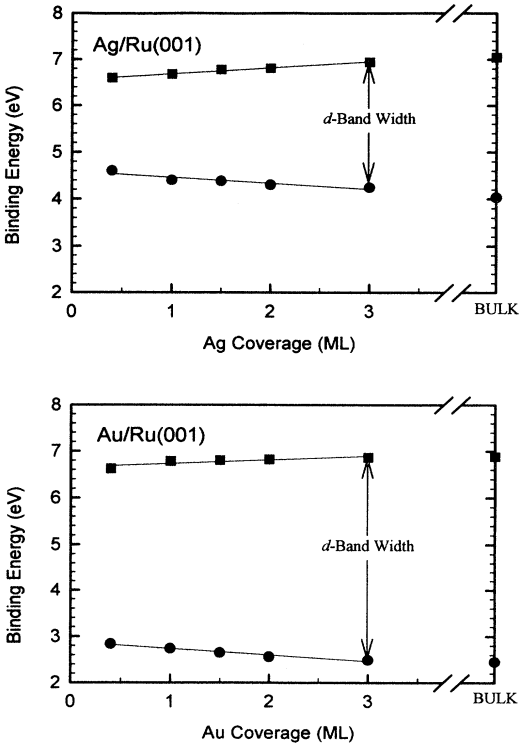

FIG. 3. Plot of the *d*-band edge positions vs coverage for both Ag/Ru (top) and Au/Ru (bottom).

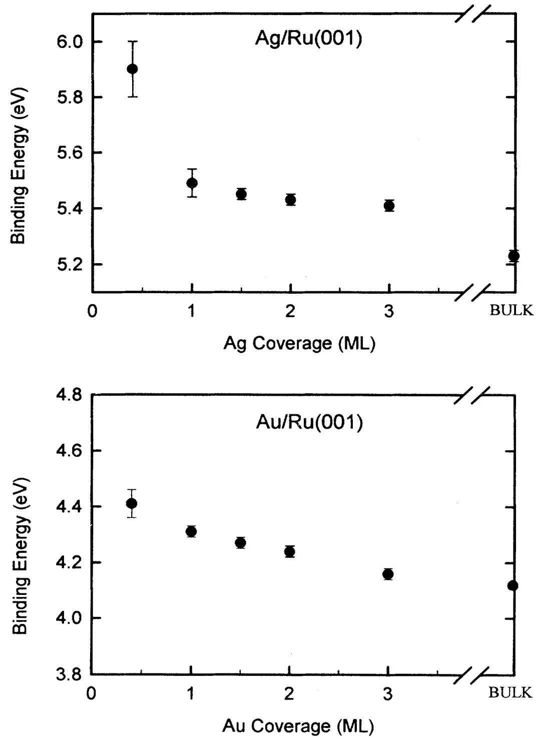

FIG. 4. Plot of the *d*-band centroid position vs coverage for both Ag/Ru (top) and Au/Ru (bottom). The binding-energy scales for both graphs is identical. The centroid position bisects the integrated area under the *d* band.

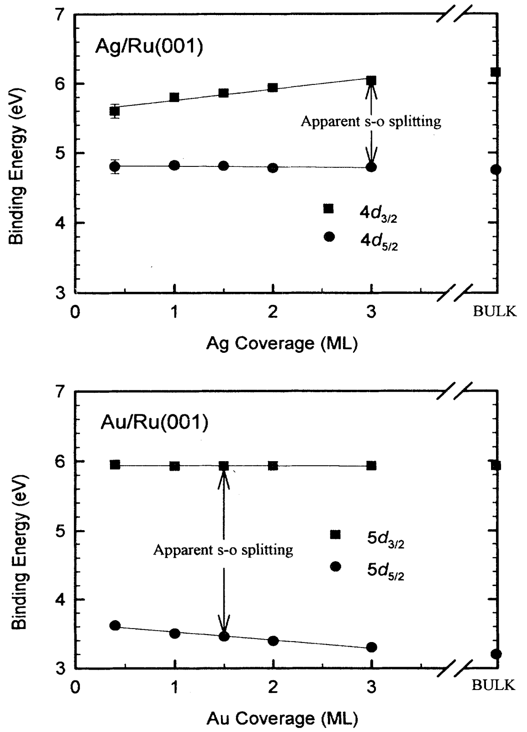

FIG. 5. Plot of the position of the *d*-band doublet maxima vs the coverage for both Ag/Ru (top) and Au/Ru (bottom). The difference between the top and the bottom values is the apparent spin-orbit splitting.

rived from Figs. 1 and 2 as a function of coverage: (a) the position (binding energy in eV) of the top and the bottom of the *d* band from which the bandwidth can be estimated; (b) the position of the centroid of the *d* band, and (c) the apparent spin-orbit splitting (position of the 5/2 and 3/2 *d*-component signatures). The experimental *d*-band widths of the overlayers are defined here as the distance between the point of inflection of the rising edge of the top and the bottom of the band. This procedure may underestimate the bandwidth but, as far as qualitative comparison is concerned, this is adequate since it compensates for the instrumental resolution somewhat. The apparent spin-orbit splitting is defined as the difference in the energy position of the split *d* bands at maximum intensity. This will vary only slightly depending on the photon energy (slightly different cross section). It should be noted that for a free gold atom, the spin-orbit splitting is 1.52 eV, for bulk Au metal, the apparent spin-orbit splitting, which involves band broadening as well as spin-orbit contributions, is ~2.7 eV. For Ag, the corresponding free atom/ion ratio and the bulk metal values are 0.55/0.57 and ~1.3 eV, respectively.[20]

B. Au/Ru(001)

Let us first concentrate on the Au/Ru(001) system. At submonolayer coverage (0.4 ML), both the bandwidth and the apparent spin-orbit splitting Δ (2.3–2.4 eV) have narrowed considerably compared to the bulk value ($\Delta=2.7$ eV), although they are nowhere near that of the atomic spin-orbit value ($\Delta_{\text{s.o.}}=1.52$ eV). This observation indicates that the adatoms are not isolated at this submonolayer coverage, and is consistent with the formation of two-dimensional islands inferred from scanning tunnel microscope[11] and photoemission results.[6]

From 1- to 3-ML coverage, the bandwidth and the apparent spin-orbit splitting increase steadily towards the bulk value, while the centroid of the *d* band shifts towards the Fermi level (decreasing binding). Shifts in the corresponding Au $4f$ level depends on whether it is measured with respect to the interior of bulk Au or to its surface. As we noted above, the 0.4-ML and 1-ML adlayers show increased binding relative to the Au surface. This binding energy increase is of the same sign and greater in magnitude than Au *d*-band shifts of Fig. 4.

Changes in the apparent spin-orbit splitting as a function of coverage differ slightly from a previous finding at lower photon energy[6] in which turnon of the bulklike spin-orbit splitting from submonolayer to multilayer coverage is more abrupt (2.3–2.5 eV) than what is observed here (2.3–2.4 eV), but the overall trends are the same; that is, the apparent spin-orbit splitting and bandwidth are nearly bulklike at 1-ML coverage and reach a bulk value at 3 ML. Of particular interest is the movement of the energy position of the *d*-band doublets: the position of the quasi $d_{3/2}$ component remains unchanged while the $d_{5/2}$ component moves towards the Fermi level as the coverage increases. This movement, together with the increasing intensity of the Au $5d_{5/2}$ component, accounts for the movement of the centroid of the *d* band towards the Fermi level from submonolayer to multilayer coverage.

C. Ag/Ru(001)

We next turn to the Ag/Ru(001) results. It can be seen from Figs. 3–5 that they follow more or less the same trend as Au/Ru(001) except that the *d*-band movement is less dramatic than in the case of Au. As was the case for Au, the conventional XPS core-level shifts of the Ag 3*d* relative to bulk Ag increase from submonolayer to multilayer coverages, while the centroid of the Ag *d* band shifts slightly towards the Fermi level, although the latter shift is barely noticeable, unlike that of Au. The reported XPS Ag 3*d* core-level shift between monolayer and multilayer (bulklike) of Ag on Ru(001) is $-0.073(1)$ (Ref. 7), while the surface-atom core-level shift of Ag is $-0.076(3)$ relative to bulk Ag, a trend similar to that of Au. Ideally, one would like to compare the adlayer valence-band spectrum with that for a surface layer of an elemental material. Unfortunately, unlike core-level spectra, this is extremely difficult experimentally[21] and one must, perforce, compare the adlayer spectrum with that of the bulk reference material bearing in mind that the valence *d*-band width of surface layer is expected to be slightly narrower than that of the bulk and its centroid shifts towards the Fermi level.[21] The *d*-band movements are the same as for Au/Ru(001) in that the apparent spin-orbit splitting increases from submonolayer to monolayer and the bandwidth increases towards the bulk value. There is one outstanding exception, however. That is that the position of the quasi $4d_{5/2}$ component remains unchanged while the $4d_{3/2}$ component moves away from the Fermi level. This is in contrast to the behavior of the Au *d*-band movement and can be interpreted in terms of the interplay of spin-orbit and band-formation considerations. Despite the inward movement (away from the Fermi level) of the $4d_{3/2}$ maximum at increasing coverage from monolayer to multilayer, the centroid of the *d* band continues to shift, albeit only slightly, towards the Fermi level with the exception of 0.5 ML where the shift is the largest and the uncertainty in its value the greatest. The *d*-band centroid shift arises because the intensity (densities of states) of the $4d_{5/2}$ component increases more rapidly than that of the $4d_{3/2}$ component as the coverage increases from submonolayer to multilayer.

D. Correlation of apparent spin-orbit splitting with bandwidth and the role of Ru

It has been recognized for some time that while the valence *d*-level splitting between metal and atom need not be identical, it is not expected to change by a factor of 2 as observed in the case of noble metals if that change is due to spin-orbit effects alone. It is true that the valence *d* electrons are somewhat contracted in the metal in the sense that they are arguably renormalized to the Wigner-Seitz (W-S) cell but the free-atom *d* charge of a Au or Ag atom $[d^9(sp)^x]$ has somewhat less than 10% of its charge outside the W-S cell; bringing this inside can then only increase the spin-orbit splitting $\Delta_{\text{s.o.}}$ by $\sim 10\%$.[22] The failure of the spectra to have the correct $d_{3/2}-d_{5/2}$ spin-orbit intensity ratio indicates that other factors are at play.

As was discussed earlier, the apparent spin-orbit splitting (separation between the *d*-band doublet) Δ may be crudely expressed as $\Delta=\sqrt{(\Delta^2_{\text{s.o.}}+\Delta^2_{\text{band}})}$, where $\Delta_{\text{s.o.}}$ is the atomic spin-orbit splitting and Δ_{band} is the band-broadening contribution. Using values given in Fig. 5, we have obtained Δ_{band} values for bulk and the thin-layer limit in our experiments of 1.28 and 0.62 eV, respectively, for Ag, and 2.35 and 1.72 eV, respectively, for Au. The Ag values indicate a factor of 2 reduction in the band-broadening contribution; this roughly scales with factor of 2 decrease in the number of Ag nearest neighbors on going from bulk to a close-packed monolayer. The Au values decrease by a factor of $\frac{2}{3}$. This suggests that something more than Au-Au interactions are contributing to the thin-layer splittings: the Au and Ru *d* bands overlap more than do Ru's with Ag's, and it is plausible that Au-Ru *d* hybridization is contributing to the splitting. This notion is entirely consistent with the much stronger Au-Ru interaction compared with that of Ag-Ru, as deduced from the heat of adsorption obtained from thermal-desorption measurements,[23] and the observation of adsorbate-induced states at low photon energy.[6] Applying the same sort of argument to the overall bandwidths of Fig. 3, would yield even weaker decreases in Δ_{band} on going to the thin-layer limit and would suggest greater substrate contributions to the noble-metal *d*-band broadening. The pseudomorphic Au and Ag layers have reduced Au-Au and Ag-Ag distance relative to those in the elemental metals. This acts to increase Δ_{band} and, hence, somewhat reduce the apparent role of substrate broadening. The doublet splittings may be a somewhat better measure of the effect since they are not affected by instrumental broadening.

E. Comparison of adlayer-substrate interaction with bulk alloying

It is found that on going from a multilayer (bulklike) to monolayer coverage the noble-metal (Au and Ag) overlayer *d* band exhibits several features: *d*-band narrowing, accompanying decreased quasi-spin-orbit splitting, and a *d*-band centroid shift away from the Fermi level. Similar trends are seen from bulk noble-metal–transition-metal alloys. There is an important difference, however, between the bulk alloys where the majority of nearest neighbors tend to be unlike neighbors and the close-packed adlayers where there are the same number of like and unlike neighbors. One manifestation of this may be in the comparison of Au's *d* band and core 4*f*-level shifts. Compared with bulk Au, the adlayer 4*f*-levels shift to weaker binding while compared with the surface of bulk Au the 4*f* shifts are to greater binding and the magnitude of this binding shift is slightly greater than that of the *d* bands. In contrast, bulk Au alloys generally show increased binding of both 4*f* and *d* bands with the increase greater for the *d* bands. As was discussed in Sec. II, the *d* bands sustain a level shift to increased binding due to the hybridization of unoccupied states of the other atomic constituent into the occupied *d* bands. This competes with the tendency for any change in local noble-metal site potential to contribute a larger shift for the more compact core level than for the less compact *d*-band electrons. It would appear that the hybridization shift predominates in the bulk alloys and not in the adlayers with their fewer unlike nearest neighbors. The core-level and valence *d*-band shifts suggest differences in substrate adlayer bonding than are encountered in other bulk-alloy systems. This warrants further investigation.

Evidence of substrate-adlayer bonding is also to be found in the limited nature of the *d*-band narrowing. Au and Ag, with their *d*-band doublet structure, offer a particularly good opportunity for monitoring the narrowing. It is reasonable to assume that the intrinsic *d*-band broadening Δ_{band} varies with the number of nearest neighbors actually involved in the *d*-band structure. The close-packed adlayers have half the number of noble-metal nearest neighbors and, consistent with this, the Ag adlayer Δ_{band} is half that of the bulk. For Au, the adlayer Δ_{band} is greater than a half suggesting that the Ru substrate actively contributes to the Au *d*-band width. This trend is plausible since the bands of Au and Ru overlap more heavily than do those of Ag and Ru.

It is also interesting to discuss the noble-metal-Ru interaction from a thermodynamic perspective, since neither Ag nor Au forms alloys with Ru in the bulk as is indicated by their phase diagram.[24] Despite this, both noble metals have surface energy sufficiently less than that of Ru; they will wet Ru readily. This is because the system is prepared to pay the cost of increasing Ru-noble-metal interaction in order to save on surface energy. The Cu-Ru bimetallic aggregate[25,26] is an excellent example of this situation. There is a tendency for Au to more readily alloy with elements in the middle of the transition-metal rows than Ag and this can be seen in Figs. 1 and 2: Au more readily covers Ru than does Ag as is shown by the fact that the Ru-like features of the spectra disappear at lower coverage, suggesting better wetting, when Au is the adatom.

In closing, the photoemission results of this paper are consistent with and augment a picture of bonding trends of noble metals with Ru. Stronger bonding is found for Au versus Ag and difference from what would occur for bulk alloying arise because of a different balance of like versus unlike nearest neighbors in an adlayer. These matters deserve further investigation.

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