

## Electronic structure of Au-Ag bimetallics: Surface alloying on Ru(001)

A. Bzowski,\* M. Kuhn,† and T. K. Sham

*Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7*

J. A. Rodriguez and J. Hrbek

*Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973*

(Received 10 June 1998; revised manuscript received 25 September 1998)

We report a study of the electronic structure of Au-Ag overlayers (total coverage varies from 2 to 9 ML) supported on Ru(001). Photoemission spectroscopy with synchrotron radiation and a Mg  $K\alpha$  x-ray source has been used to study the valence band and the Au 4*f* and Ag 3*d* core levels of these systems. It is found that, in most cases, two-dimensional alloy formation occurs upon deposition at room temperature. The extent of surface alloying depends on the order of deposition, composition, thickness, and annealing temperature. By comparing the valence band and binding energy shifts for bulk and surface alloys, we found that both systems exhibit the same trend: that is, that relative to the *d* band of pure Au, the alloy *d* band narrows and the Au 4*f* shifts to higher binding energy upon decreasing Au concentration. However, the surface alloy *d* band is consistently narrower than that of the bulk with the same stoichiometry. Similar surface bulk behavior is also seen in the Au 4*f* binding energy shift and the Au *d*-band doublets. This behavior is attributed to the two-dimensional nature (reduction in coordination number of like nearest neighbors on average) of the surface alloy. [S0163-1829(99)01211-4]

### I. INTRODUCTION

Au and Ag are prototype noble metals with fcc structure and nominally filled *d* bands, which exhibit an unmistakable spin-orbit splitting signature in their photoemission valence-band spectrum. Au and Ag are completely miscible in the solid state and form fcc alloys. Despite extensive literature on the Au-Ag alloy system, it continues to be investigated in connection with Friedel charge screening<sup>1,2</sup> and charge redistribution studies,<sup>3-12</sup> as new materials and much improved characterization and computational techniques become available. One area of interest is the electronic structure of Au-Ag bimetallics in low-dimensional systems such as overlayers, interfaces, and nanostructures. It is, therefore, of considerable interest to study the two-dimensional alloy of Au and Ag overlayers on an “inert” single-crystal substrate. Here “inert” merely refers to the absence of surface compound formation and interdiffusion between the adsorbate (Au and Ag) and the substrate. In fact, the interaction between the adlayer and the substrate must be strong enough to hold the adlayer two dimensional.

Ru(001) crystal was used as the substrate for several reasons. First, its hcp(001) face is a close-packed surface with the same two-dimensional (2D) packing of atoms as the *fcc*(111) structure of those of Au, Ag, and Au-Ag alloys. Second, both Au and Ag wet the Ru surface, but neither forms alloys with Ru nor diffuses into the Ru(001) substrate. The growth mode of Au and Ag on Ru(001) is pseudomorphic<sup>13-15</sup> (overlayers adopt a structure that matches that of the substrate) and follows a Stranski-Krastanov (SK) growth mechanism, although in the case of Ag, the first layer does not appear to be filled until the coverage reaches  $\sim 1.5$  ML.<sup>13</sup> Third, the adsorption characteristics of Au and Ag layers individually on Ru(001) have been well characterized with layer-resolved photoemission and

thermal-desorption spectroscopy (TDS).<sup>13-15</sup>

It has been established that both Au and Ag are somewhat compressed within the layers in the pseudomorphic regime since both Au and Ag have larger metallic radii than Ru. At submonolayer coverage Au, for example, forms dendritic two-dimensional islands instead of isolated Au atoms.<sup>16</sup> The lower surface energies of Au and Ag compared to Ru make them energetically favorable to wet the Ru substrate without forming an alloy with Ru in the bulk. Thus, Ru(001) provides a template for the study of 2D alloying of Au and Ag in that it facilitates alloying by keeping the first layer adsorbates two dimensional.

Photoemission was used in this paper because of its sensitivity to changes in the core level and the Au and Ag *d* bands, especially the top of the Au *d* band (“*d*<sub>5/2</sub>” component).<sup>10</sup> Small changes in the electronic structure upon alloying can often be revealed by photoemission measurements of the valence band with synchrotron radiation.<sup>10,14,15</sup> It is well established that the Au-Au *d-d* interaction in bulk Au is very strong. Any attempt to reduce this interaction, such as alloying, will reduce the intrinsic Au *d*-band-width and the associated *d*-band doublet (the separation between the two *d*-band maxima of Au origin, henceforth denoted “apparent spin-orbit splitting,”<sup>17,18</sup>) and pushes the centroid of the Au *d*-band component away from the Fermi level. This trend is accompanied by a Au 4*f* core-level shift away from the Fermi level. Furthermore, photoemission studies of pure Au and Ag overlayers<sup>15</sup> show that the noble metal overlayers exhibit essentially the same characteristics as those of the bulk metal except that the width of the *d* band is narrower at low coverage as a result of a reduction in the average coordination number.<sup>15</sup>

The objective of this paper is to investigate changes in the electronic structure and interaction of the Au and Ag coadsorbates as a function of overlayer thickness, order of depo-

sition, and annealing temperature. Photoemission spectroscopy with synchrotron radiation and conventional x-ray photoelectron spectroscopy (XPS) were used to study the valence band as well as the Au  $4f$  and Ag  $3d$  core-level binding energy shifts of coadsorbed Au and Ag overlayers on Ru(001) at monolayer to multilayer coverage. The coverage was monitored by thermal desorption measurements. The results will be compared with those of bulk alloys.

There have been several papers<sup>7-9,13</sup> on the interaction of Au and Ag overlayers on Ru(001) suggesting that under certain conditions, depending on the coverage and temperature, Au-Ag alloying occurs on the surface. However, most of these investigations were based on TDS, which provides the adsorption energetic but does not give direct information on the electronic structure of the adsorbates. In bulk alloys, it has been shown from Mössbauer,<sup>3,4</sup> photoemission and x-ray absorption near-edge structure<sup>5,19-21</sup> studies that significant charge redistribution in Au-Ag alloys occurs, and it can be described with a charge-compensation mechanism.<sup>5</sup> It is postulated that Au loses  $d$  and gains  $s$  electrons, while Ag gains  $d$  and loses  $s$  electron; the overall charge flow is small ( $\sim 0.1 e$  count typical) and is onto Au, the most electronegative metallic element. This is in accord with electroneutrality (in metallic systems, the atomic site in an alloy tends to maintain charge neutrality locally, site refers to the Wigner-Seitz volume) and electronegativity considerations. Using this mechanism, we can explain the results obtained for Au and Ag deposited on a Ru(001) surface as a function of coverage in terms of 2D alloying.

The experimental procedures are given in Sec. II. Results and discussion are presented in Sec. III in five subsections. In Sec. III A we report the results for a system consisting of one monolayer each ( $\theta_{\text{Au}} = \theta_{\text{Ag}} = 1 \text{ ML}$ ) of Au and Ag on Ru(001) as a function of the order of deposition and annealing temperatures. The photoemission systematics for a series of Ag/Au/Ru [i.e., Au was deposited first on the Ru(001) substrate followed by Ag] at various compositions (from 67 to 11 at. % of Au with overall coverage of 2 to 9 overlayers) are presented in Sec. III B, where the effect of the adlayer thickness (1–2 ML of Au plus one to multilayers of Ag) and stoichiometry are also examined. This is followed in Sec. III C by a study of a Au/Ag/Ru system prepared by deposition in the reversed order (Ag deposited first followed by Au). The two systems are compared in Sec. III D. In all these discussions, Au  $4f$  and Ag  $3d$  binding-energy shifts and the valence band were used to monitor the interaction between the noble metals. Emphasis was placed on the features of the valence band such as the changes in the  $d$ -band-width, centroid position, and apparent spin-orbit splitting of the “Au  $d$  band”. All of these gauges have been used to study the extent of alloying according to the charge-compensation model for both the bulk and surface alloys of same composition. Section III E presents the electronic structure difference between bulk and surface Au-Ag systems and its interpretation. Conclusions are given in Sec. IV.

## II. EXPERIMENT

Gold and silver overlayers were prepared *in situ* by evaporation of the desired metal onto a clean Ru(001) substrate. During each deposition, the evaporation rate of the

dosers was monitored with a mass spectrometer. We found that using a mass spectrometer is the most reliable way to monitor the deposition rate. Coverage were checked with TDS at the end of the run. The surface of the Ru(001) crystal was cleaned using standard procedures. The crystal was protected with a thick layer of Au at the end of the day.

Measurements reported here were performed using three different UHV systems. The valence band and high-resolution Au  $4f$  core-level photoemission experiments were carried out at the Canadian Synchrotron Radiation Facility (CSRF) located at the Synchrotron Radiation Center (Aladdin), University of Wisconsin-Madison. An ultrahigh vacuum chamber (base pressure  $\leq 4 \times 10^{-10}$  Torr) equipped with low-energy electron diffraction optics, ion sputter gun, quadrupole mass spectrometer, and a Leybold hemispherical electron-energy analyzer was used. Photoemission experiments were performed in an angle-integrated mode using the CSRF grasshopper monochromator with a 1800 gr/mm grating. To optimize cross section and resolution, a photon energy of 170 eV was used for the Au  $4f$  core levels and 70 eV for the valence-band studies. The overall energy resolution for the Au  $4f$  is  $\sim 0.3$  eV. All photoemission spectra were normalized to the photon flux ( $I_0$ ) monitored by a Ni mesh.

Ag  $3d$  XPS measurements were made at Brookhaven National Laboratory using a Mg  $K\alpha$  source at a base pressure of  $\sim 1 \times 10^{-10}$  Torr and a VSW-150 hemispherical electron-energy analyzer (with a multichannel detector). TDS measurements were performed in a multiple-mass mode with a UTI quadrupole mass spectrometer and a Tekniven data acquisition system. A temperature range of 600–1500 K and a constant heating rate of 2 K/s were used throughout. A TDS was taken following each photoemission experiment at the synchrotron to confirm the amount of material deposited. This was done by integrating the area under the desorption peak for each sample and then comparing it to the data for 1 ML of the pure metal on Ru taken at the start of each day.

All core-level and valence-band binding energies were referenced to the Fermi level ( $E_F$ ). The location of the upper and lower edges of the valence  $d$  bands were found by differentiating each curve and finding the corresponding points of inflection. Positions of the Au  $d$ -band maxima, which vary considerably in the alloys, were obtained by subtracting the contribution from the Ag  $d$  band, which varies relatively little.<sup>10</sup> The justification for this procedure is based on the observation of the bulk alloy  $d$  band, which shows that upon Au-Ag alloy formation, the Ag  $d$  band and the Au  $d_{3/2}$  component move relatively little compared to the Au “ $d_{5/2}$ ” component. Thus, an accompanying alternate gauge for alloying is the shift of the position of the top of the alloy  $d$  band, which is of primarily Au character and does not overlap significantly with the Ag  $d$  band in energy. The alloy  $d$  band centroid positions were located by bisecting the integrated area under the overall  $d$  band between the points of inflection of the rising and falling edges. Core-level data were fitted with a many-body line shape.

## III. RESULTS AND DISCUSSION

### A. 1 ML Au and 1 ML Ag codeposited on Ru(001)

Figure 1 shows the valence-band photoemission spectra of 1 ML each of Au and Ag on Ru(001) prepared under

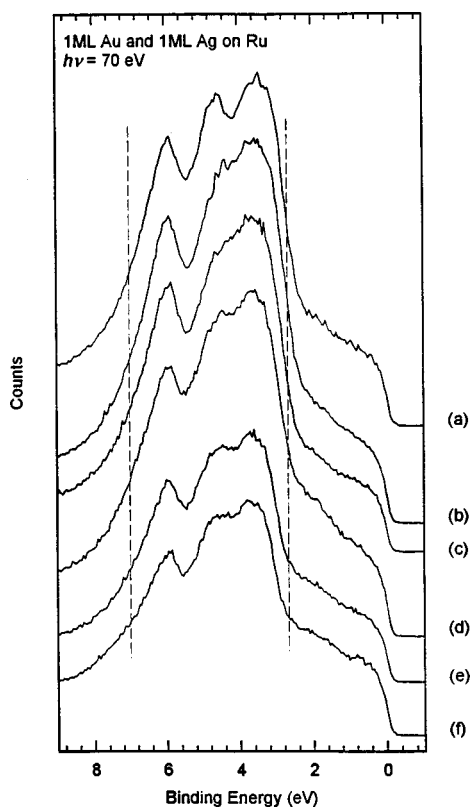


FIG. 1. Valence-band spectra for (a) sum of 1 ML Au/Ru and 1 ML Ag/Ru, (b) 1 ML Ag/1 ML Au/Ru, Au first, as-deposited, (c) Ag/Au/Ru annealed at 600 K for 5 min, (d) 1 ML Au/1 ML Ag/Ru, Ag first as-deposited; (e) Au/Ag/Ru annealed at 600 K for 5 min and (f) at 800 K for 5 min. The vertical lines mark the position of the top and the bottom of the  $d$  band in (a).

different conditions, together with the sum of the spectra for 1 ML Au on Ru(001) and 1 ML Ag on Ru(001). Au/Ag/Ru henceforth denotes 1 ML of Ag deposited first on a clean Ru substrate followed by 1 ML of Au and vice versa for Ag/Au/Ru; both at room temperature. Figure 1(a) depicts a valence-band spectrum of the sum of normalized 1 ML Au/Ru and 1 ML Ag/Ru spectra. The individual 1 ML Au and Ag spectra have been described previously<sup>15</sup> (they simply exhibit the same characteristics of the  $d$  band of the pure element with a slightly narrower band width). To compensate for the extra substrate signal, a Ru background was subtracted from the Ag/Ru spectrum prior to addition.<sup>15</sup> It should be noted that for the pure metals, the  $d$  band widens as the coverage increases from monolayer to multilayer, and this is accompanied by an increase of the apparent spin-orbit splitting towards the bulk value. This is largely due to the movement of the  $5d_{5/2}$  component towards the Fermi level in the case of Au and the  $4d_{3/2}$  component away from the Fermi level in the case of Ag. This behavior together with the behavior of the  $d$  bands in bulk alloys<sup>10,11</sup> will be used to interpret the valence-band results of the surface alloys. In the following we use interfacial interaction, intermixing, and surface alloying to describe the interaction among Au, Ag, and the Ru substrate. Interfacial interaction refers to the interaction of two layers in contact with no compound formation or interdiffusion. Intermixing refers to a metastable state where some intermixing of atoms in both layers occurs, while surface alloying implies the formation of a homogeneous phase of Au-Ag alloy on Ru.

Thus, Fig. 1(a) represents the overall appearance of the valence band if no Au-Ag interaction of any kind takes place in the system with 1 ML Au and Ag, i.e., the Au and Ag adlayers were just in contact with each other with no interfacial interaction, intermixing, or island formation. Notice that three distinctive  $d$ -band components can be seen in the sum spectrum. They can be easily assigned to the Au and Ag components, based on the original spectra of 1 ML Au/Ru and 1 ML Ag/Ru. For example, the first and second peak closest to the Fermi level are primary of Au and Ag character, respectively. It is also interesting to note that the Ru substrate signal is almost totally suppressed in Au/Ru, but is only partially suppressed in Ag/Ru. The implication of this difference will be discussed below. The “Au  $5d$  band” apparent spin-orbit splitting, the centroid position of the  $d$  band, and the overall width of the  $d$  band together with core-level measurements will be used to monitor surface alloying.

It can be seen from Fig. 1 that there is little noticeable movement of the top of the  $d$  band for the Ag/Au/Ru system (Au first) for both the as-deposited and the annealed at 600 K samples [Figs. 1(b) and 1(c)]. However, the as-deposited Au/Ag/Ru, (Ag first) exhibits a slight but unmistakable  $d$ -band narrowing [Fig. 1(d)] as can be seen in the inward movement of the top of the  $d$  band. Further narrowing, which is again most noticeable from the shift of the rising edge of the top of the  $d$  band (primarily of Au character), occurred when the sample was annealed at 600 K for 5 min. No further narrowing was observed when the Au/Ag/Ru sample was annealed at 800 K for 5 min, although the Ru signal (closer to the Fermi level) became more noticeable. This indicates that 3D islands are formed revealing some of the underlying Ru substrate. Along with the narrowing of the overall  $d$  band was a shift of the  $d$ -band centroid to a higher binding energy in the Au/Ag/Ru system. Previous studies of bulk Au-Ag alloys<sup>6,10,11,20</sup> showed that there is a narrowing of the overall alloy  $d$  band on going from pure Au to dilute Au-Ag alloys, although the narrowing is less noticeable for composition with more than 50% Au. A series of valence-band spectra for bulk alloys using laboratory XPS (resolution  $\sim 0.9$  eV at 1253.8 eV photon energy) and synchrotron radiation ( $\sim 0.2$  eV resolution at 70 eV photon energy, same experimental conditions as those used to record the surface alloy spectra) are shown in Figs. 2(a) and 2(b), respectively. It should be noted that despite some Ag-Au  $d$ - $d$  interaction (broadening), the individual  $d$ -band characters remain.

The  $d$ -band narrowing is more apparent in the synchrotron data as the result of better instrumental resolution. This is accompanied by a shift of the centroid of the  $d$  band away from the Fermi level and a reduction in the “Au  $5d$ ” apparent spin-orbit splitting. In pure Au metal, this splitting is 2.72 eV considerably larger than the atomic value of 1.52 eV. This apparent spin-orbit splitting arises from the combined effects of spin-orbit interaction and band formation. This splitting reduces upon dilution (and in some cases approaches the atomic value) as the Au  $d$ - $d$  interaction is reduced and the coordination number of like atoms decreases. It has been useful to follow the separation of this doublet  $\Delta$  in terms of the quadrature contribution of the  $d$ -band term  $\Delta_{\text{band}}$  (sensitive to alloying) and the atomic spin-orbit splitting  $\Delta_{s.o.}$  (1.52 eV for Au atom).<sup>10,15</sup>

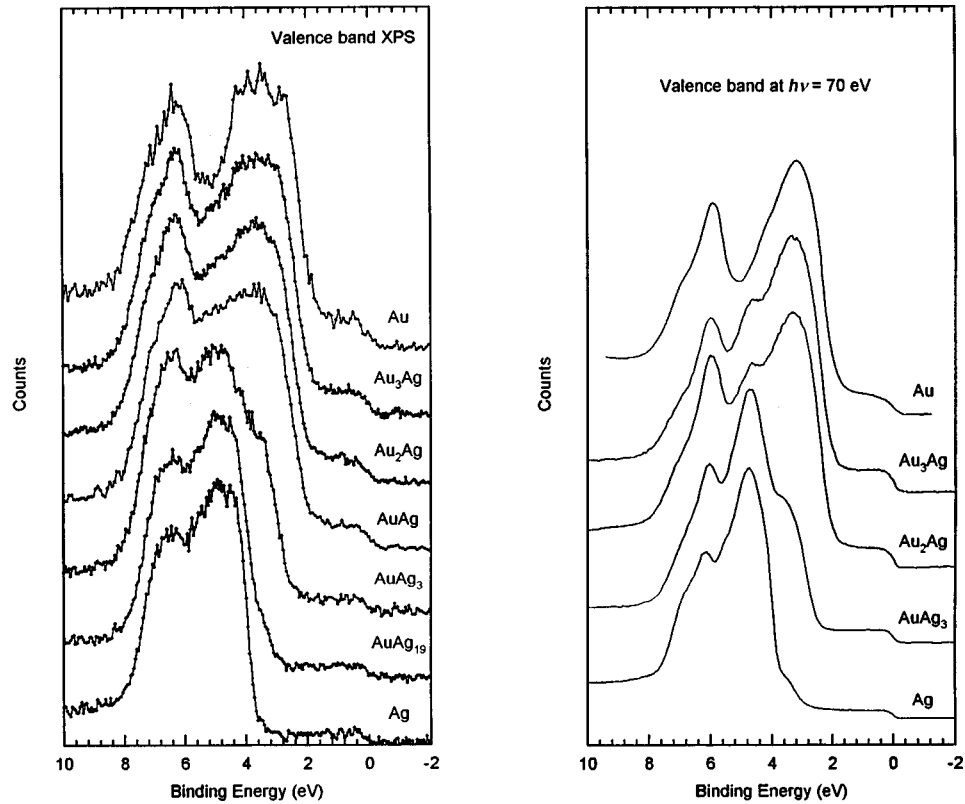


FIG. 2. Valence band for a series of Au-Ag alloys with 1486.6-eV photons (left panel) and 70-eV photons (right panel); the subscripts denote composition. The slight variation between them is due to cross section and energy resolution difference.

$$\Delta = \sqrt{\Delta_{\text{band}}^2 + \Delta_{s.o.}^2} \quad (1)$$

The overall  $d$  bandwidth of the alloy, which is also related to the band term in the above expression, gives perhaps the most direct qualitative indication of alloying since it is associated with the reduction in the Au-Au  $5d$  interaction (movement of the  $5d_{5/2}$  component). This phenomenon has been observed for a variety of other alloys of Au,<sup>17,18</sup> although for Au-Ag alloys, the reduction is small and more gradual for high Au concentration and more apparent for low Au concentration alloys. Thus, by monitoring the width of the overall  $d$  band, the apparent spin-orbit splitting of the Au component, the position of the centroid of the valence band, and the Au  $4f$  binding energy, one can determine the nature of the Au-Ag interaction on Ru(001) with confidence.

Based on the above described method of analysis, our results clearly indicate a reduction in Au  $d$ - $d$  interaction in the Au/Ag/Ru samples. This narrowing ( $\sim 0.3$  eV) and the accompanying centroid shift of  $\sim 0.1$  eV for the Au/Ag/Ru(001) system relative to the sum spectrum are in good accord with bulk studies and suggest that alloying has taken place. It should be noted that there is little noticeable  $d$ -band narrowing for the Ag/Au/Ru coverage with respect to the sum spectrum. A more detailed comparison between the representative spectra is shown in Fig. 3, which contrasts the Ag/Au/Ru sample annealed at 600 K with that of the Au/Ag/Ru sample annealed at 800 K. A difference in the overall  $d$  bandwidth of  $\sim 0.3$  eV is readily seen. This difference is mainly due to the movement of the upper edge of the band away from the Fermi level (towards a higher binding energy). There is also a reduction in the apparent spin-orbit

splitting of the “Au  $d$ -band” maxima. Furthermore, the Au/Ag/Ru spectrum shows an increased Ru signal near the Fermi level (0–3 eV binding energy). These observations suggest that there are differences in the degree of interaction between Au and Ag depending on which was deposited first (in contact with the substrate). Although Au-Ag 2D alloy formation seems to be taking place only when Ag is deposited first on Ru, interaction of Au and Ag adlayers at the interface in the Ag/Au/Ru system does occur. In fact, Fig. 1 clearly shows that the Au and Ag  $d$ -band peaks broaden noticeably compared to the sum (noninteracting Au-Ag) spectrum, which exhibits three sharp peaks. This observation in-

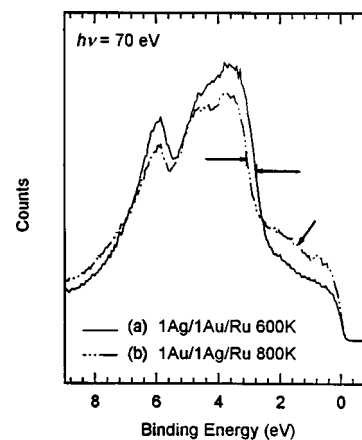


FIG. 3. Valence-band spectra of the valence-band region of 1 ML Ag/1 ML Au/Ru annealed at 600 K for 5 min and (b) 1 ML Au/1 ML Ag/Ru annealed at 800 K for 5 min.

TABLE I. (a) Au  $4f_{7/2}$  core-level positions for the Ag/Au/Ru(001): as-deposited and annealed to 600 K; (b) Ag  $3d_{5/2}$  core-level positions for the Ag/Au/Ru(001): as-deposited and annealed to 700 K.

(a)				
Coverage	$E_B$ Au $4f_{7/2}$ ( $\pm 0.03$ eV)		$\Delta E_B$ Au $4f_{7/2}$ <sup>a</sup> ( $\pm 0.04$ eV)	
	As-deposited	Annealed at 600 K	As-deposited	Annealed at 600 K
1 ML Au/Ru	83.77			
Ag/2Au/Ru	83.72	83.72	-0.05	-0.05
Ag/Au/Ru	83.77	83.80	0.00	0.03
3Ag/Au/Ru	83.86	83.88	0.09	0.11
8Ag/Au/Ru	83.91	83.89	0.14	0.12

<sup>a</sup>Changes are relative to 1 ML Au/Ru(001).

(b)				
Coverage	$E_B$ Ag $3d_{5/2}$ <sup>a</sup> ( $\pm 0.05$ eV)		$\Delta E_B$ Ag $3d_{5/2}$ <sup>b</sup> ( $\pm 0.07$ eV)	
	As-deposited	Annealed at 700 K	As-deposited	Annealed at 700 K
1 ML Ag/Ru	368.05 (1633)			
3 Ag/Au/Ru	368.11 (5729)	368.09 (5680)	0.06	0.04
Ag/Au/Ru	367.99 (2538)	368.00 (2432)	-0.06	-0.05
Ag/2.5Au/Ru	368.00 (1069)	367.94 (1024)	-0.05	-0.11
Ag/3Au/Ru	368.02 (1636)	367.98 (1477)	-0.03	-0.07

<sup>b</sup>Numbers in parentheses represent the total area under each peak.  
<sup>c</sup>Changes are relative to 1 ML Ag/Ru(001).

icates that despite the lack of intermixing and alloying, there is modest electronic interaction between Au and Ag atoms at the Ag-Au interface in the Ag/Au/Ru system. We recall that alloying refers to intermixing of Au and Ag atoms forming a stable homogeneous phase on Ru(001).

More information about the intermixing of Au and Ag and alloy formation can be obtained from the Au  $4f$  core-level shifts. It has been established that along with the narrowing of the alloy  $d$  band, the accompanying shifts of the Au  $4f$  core level to a higher binding energy and Ag  $3d$  to a lower binding energy are excellent indicators for alloy formation between Au and Ag [Tables I(a) and I(b)]. The as-deposited Ag/Au/Ru system exhibits no Au  $4f$  shift relative to that of 1 ML Au/Ru. It is interesting to note that the Au  $4f$  for Ag/Au/Ru is at 83.77 eV, which is between that of the surface Au on Au (83.61 eV) and bulk Au (83.92 eV).<sup>22</sup> As described in the literature, this is a result of a significant Au-Ru interfacial interaction, which will influence the behavior of the Ag/Au/Ru system. The Au  $4f$  core level moves slightly (0.03 eV) towards higher binding energy after annealing at 600 K for 5 min. This observation suggests that a stable layer-by-layer Ag/Au/Ru forms readily upon deposition. When the order of deposition is reversed (Au is dosed onto a Ag/Ru adlayer), the Au  $4f$  core-level shift is more significant (Table II). The as-deposited Au/Ag/Ru system at room temperature exhibits a 0.04-eV shift to higher binding energy relative to 1 ML Au/Ru. This shift becomes greater (0.06 eV) when the sample is annealed for 5 min at 600 K. These observations indicate that when 1 ML of Ag is deposited first on a Ru(001) substrate followed by Au, some intermixing of Au and Ag takes place readily during deposition at room temperature. Larger Au  $4f$  shifts upon annealing at higher temperature suggest alloy formation.

Thermal desorption experiments show that the desorption temperature for 1 ML of Au from Ru(001) is much higher than that of Ag from Ru(001) indicating that the Au-Ru interaction is stronger than that of Ag-Ru.<sup>23</sup> This interaction turns out to be an important factor in the Au-Ag alloying on Ru (at least in the 1-ML regime). When 1 ML of Au is deposited first on the Ru substrate it wets the entire surface. This, along with the stronger Au-Ru interaction, prevents Ag from diffusing to the Au-Ru interface through the Au layers and intermixing. The only interaction between Au and Ag is at the Ag-Au interface. The result is no alloying even at elevated temperatures. When 1 ML of Ag is dosed first, however, there has been photoemission evidence<sup>13,15</sup> showing that it does not cover the Ru surface entirely, but forms 3D islands before the first layer is completed; in fact, Ag requires  $\sim 1.5$  ML to cover the Ru surface completely (Ru substrate emission was partially suppressed in the valence-band photoemission spectrum until coverage reaches  $\sim 1.5$  ML). Thus, when Au atoms are subsequently deposited on top of the 1 ML Ag already on Ru(001) surface, they will come in contact with both the Ag overlayer and the partially exposed Ru substrate, and they begin to intermix with the Ag adsorbate. The intermixing facilitated by annealing results in the formation of a stable Au-Ag alloy on Ru(001), as indicated by the shift of the top of the  $d$  band [Figs. 1(d)–1(f)] and the positive Au  $4f$  binding energy shift predicted by the charge-compensation model and observed in bulk alloys.<sup>5,11</sup> We infer, from the much-suppressed Ru substrate signal, that the surface alloys remain largely 2D even after annealing at 800 K.

The relative intensity of the Au  $4f$  signal is also consistent with the notion of Au-Ag alloying in the Au/Ag/Ru system. The Au  $4f$  intensity for Au/Ag/Ru (600 K) is only

TABLE II. (a) Au  $4f_{7/2}$  core-level positions for the Au/Ag/Ru(001): as-deposited and annealed to 600 K; (b) Ag  $3d_{5/2}$  core-level positions for the Au/Ag/Ru(001): as-deposited and annealed to 700 K.

Coverage	$E_B$ Au $4f_{7/2}$ ( $\pm 0.03$ eV)		$\Delta E_B$ Au $4f_{7/2}$ <sup>a</sup> ( $\pm 0.04$ eV)	
	As-deposited	Annealed at 600 K	As-deposited	Annealed at 600 K
1 ML Au/Ru	83.77			
2Au/Ag/Ru	83.71	83.73	-0.06	-0.04
Au/Ag/Ru	83.81	83.83	0.04	0.06
Au/2Ag/Ru	83.79	83.88	0.02	0.11
Au/8Ag/Ru	83.81	83.90	0.04	0.13

<sup>a</sup>Changes are relative to 1 ML Au/Ru(001).

Coverage	$E_B$ Ag $3d_{5/2}$ <sup>a</sup> ( $\pm 0.05$ eV)		$\Delta E_B$ Ag $3d_{5/2}$ <sup>b</sup> ( $\pm 0.07$ eV)	
	As-deposited	Annealed at 700 K	As-deposited	Annealed at 700 K
1 ML Ag/Ru	368.05 (1633)			
Au/3Ag/Ru	368.06 (3435)	368.07 (4002)	0.01	0.02
Au/Ag/Ru	367.96 (1313)	367.94 (1513)	-0.09	-0.11
2Au/Ag/Ru	368.01 (2370)	368.00 (2398)	-0.04	-0.05
3Au/Ag/Ru	367.99 (1237)	367.98 (1227)	-0.06	-0.07

<sup>a</sup>Numbers in parentheses represent the total area under each peak.

<sup>b</sup>Changes are relative to 1 ML Ag/Ru(00).

68% of that of Au/Ru. Since these spectra were obtained with identical experimental configurations and were normalized to the photon flux, the reduction in Au  $4f$  intensity suggests that approximately half the Au atoms have diffused to the interface pushing the same number of Ag atoms up to the second layer. Consequently, this would reduce the Au  $4f$  signal from the Au atoms at the Ru interface since the escape depth of the Au  $4f$  electrons (kinetic energy  $\sim 80$  eV) is about  $7 \text{ \AA}$  according to the universal curve. Therefore, the intensity for the Au in contact with Ru would be reduced. Using these numbers and assuming a layer thickness of  $\sim 2.5 \text{ \AA}$ , we expect the reduction to be  $\sim 70\%$  for uniform mixing, in good accord with the observed 68%. It should be noted, however, that epitaxial Ag/Au/Ru, as well as segregated Ag and Au islands, would also reduce the Au  $4f$  intensity, but would not produce the observed shift.

Ag  $3d$  XPS spectra of Au-Ag overlayers on Ru(001) have been recorded with a Mg  $K\alpha$  source [Tables I(b) and II(b)]. Relative to 1 ML Ag/Ru the Ag  $3d$  peaks for the as-deposited Ag/Au/Ru sample shift to a slightly lower binding energy ( $-0.06$  eV). No change is observed upon annealing. However, for the reverse order of deposition (Ag dosed first), the shift almost doubles at room temperature ( $-0.09$  eV) and increases further ( $-0.11$  eV) upon annealing at 700 K for 5 min. This is consistent in both magnitude and direction with the shifts observed in bulk Au-Ag alloys,<sup>11,20</sup> the Ag  $3d$  core-level shift for the Au/Ag bulk sample relative to pure Ag is  $\sim -0.15$  eV. It is apparent from these shifts that for Au/Ag/Ru, a stable Au-Ag alloy has formed on the surface of the Ru(001) substrate after annealing. Furthermore, its

composition is  $\sim 50/50$  Au-Ag, the same as that of the bulk Au<sub>0.50</sub>Ag<sub>0.50</sub> alloy. It is interesting to note that the intensity of the  $3d_{5/2}$  peak for the Ag/Au/Ru sample drops by  $\sim 4\%$  [Table II(b)] after annealing, but the intensity for the Au/Ag/Ru sample increases by  $\sim 15\%$  upon annealing. The latter result strongly suggests that Ag intermixes with Au and migrates to the surface. The effect of escape depth is less noticeable here than what was seen in the Au  $4f$  spectra discussed above, because the Ag  $3d$  electrons have higher kinetic energy ( $\sim 900$  eV when excited with Mg x-rays).

Figure 4 shows typical Au and Ag thermal-desorption data for the two overlayer systems. No changes can be seen in the Au TDS data between the 1 ML Au/Ru and the two Au-Ag/Ru(001) samples. This is because by the time Au desorbs, Ag has already been evaporated. Consequently, the Au TDS spectra provide no information about the Au-Ag interactions. A distinct change can be seen from the Ag TDS, however. There is a 50-K shift towards lower desorption temperature for the coadsorbates. This indicates weaker Ag substrate interaction upon codeposition of Ag and Au on Ru relative to Ag/Ru. One can also think of the process as desorption of Ag from a Au-coated Ru(001) surface. The thermodynamics implication of such an event will be explored elsewhere.

It is interesting to compare the observations of Ag/Au/Ru and Au/Ag/Ru with those of Au/Cu/Ru, Cu/Au/Ru (Ref. 22), and Cs/Au/Ru, Au/Cs/Ru,<sup>24,25</sup> all at  $\sim 1$ -ML coverage for each adsorbate. The desorption energy for a monolayer of these metals on Ru(001) exhibits the trend of

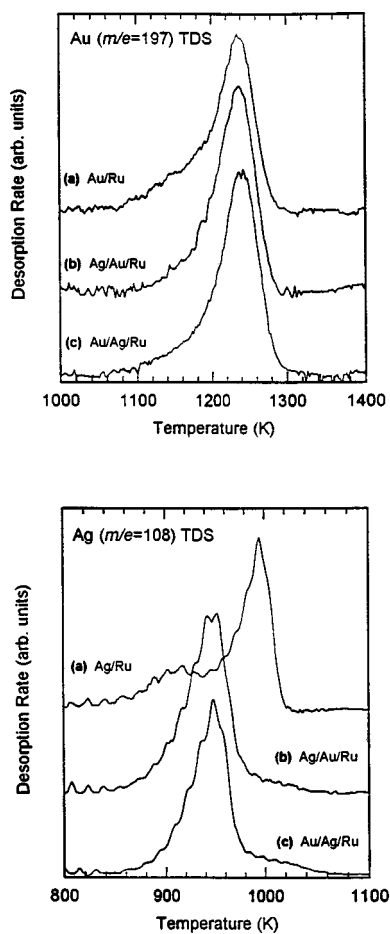


FIG. 4. Multiple-mass TDS of Au (upper panel) and Ag (lower panel) of 1 ML Au/Ru, 1 ML Ag/Ru, 1 ML Ag/1 ML Au/Ru, 1 ML Ag/1 Au ML/Ru.

Au>Cu>Ag>Cs. So far the Au-Cu systems appears to be the only one that forms 2D alloys readily at room temperature, regardless of the order of deposition.<sup>22</sup> This observation has been interpreted as a substrate-assisted 2D alloying in which the energy of alloying becomes more important than the energy of Au-Au and Au-Ru interaction. The observation of substrate assisted 2D alloying at room temperature bears some significance, since all the metals of concern here form alloys in the bulk only at elevated temperatures. Thus, the substrate will play a significant role that is that it keeps at least the first and perhaps the second layer two-dimensional (*S-K* mode). The same argument can be applied to Ag/Au/Ru(001), where the energy of Au-Ag alloying does not seem to be able to overcome the stronger Au-Au and Au-Ru interaction. This is certainly true in the case of the Au-Cs system,<sup>23,24</sup> where Cs and Au form a stable compound in the bulk, but do not alloy on Ru at these coverages. The Au/Ag/Ru system, on the other hand, behaves like Au/Cu/Ru.

It is also interesting to compare our results with those of Wandelt *et al.*,<sup>8</sup> who investigated Au and Ag interfaces on Ru(001). Based on photoemission of adsorbed xenon results they concluded that thermally, the Au/Ag interface on Ru(001) substrate is less stable than the Ag/Au interface. Our results are in agreement with this conclusion. Furthermore, using photoemission we also confirm their finding that the Au atoms penetrate into the Ag monolayer deposited on Ru,

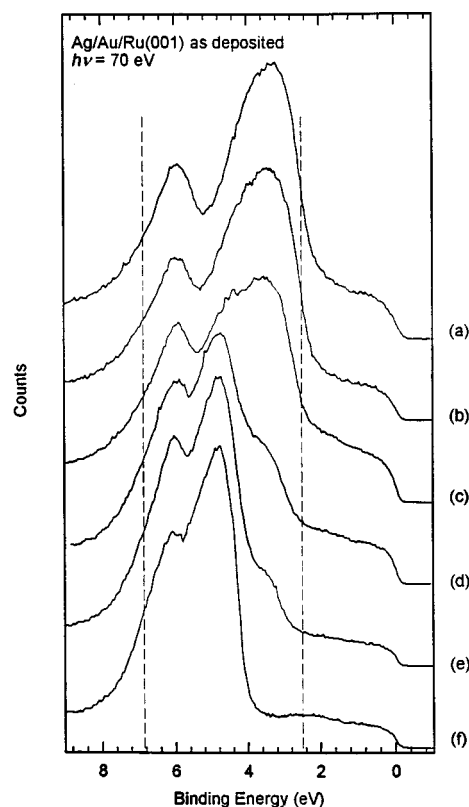


FIG. 5. Valence-band spectra for the Au first, as-deposited Ag/Au/Ru system: (a) Au(2 ML)/Ru, (b) Ag(1 ML)/Au(2 ML)/Ru, (c) Ag(1 ML)/Au(1 ML)/Ru, (d) Ag(3 ML)/Au(1 ML)/Ru, (e) Ag(8 ML)/Au(1 ML)/Ru, and (f) Ag(3 ML)/Ru. The vertical lines indicate the bandwidth of spectrum (a).

but Ag atoms do not diffuse into Au at room temperature. It should be noted that our experimental conditions pertaining to the formation of a Au-Ag alloy on Ru differ from those of Wandelt *et al.*,<sup>8</sup> who in most cases used submonolayer coverage of both metals. This difference in the coverage of the metals deposited (we dosed 1 ML where they deposited only 0.3–0.5 ML) will likely alter the mechanics of intermixing, diffusion, and alloying, as will be soon demonstrated below for multilayer coverage.

What emerges from the study of one monolayer each of Au and Ag adsorbed on Ru(001) is a picture where the order of deposition, annealing temperature, and presence of the Ru(001) substrate (difference in Au/Ru and Ag/Ru interaction) all play a crucial role in two-dimensional alloy formation. We explore below whether or not multilayer coverage exhibit similar behavior.

### B. Ag/Au/Ru(001) multilayers with Au deposited first

The notation utilized to denote the multilayers for the rest of the paper is similar to that used in the previous section. For example, 1 ML Ag/2 ML Au/Ru or simply Ag/2 Au/Ru denotes 2 ML of Au deposited onto a clean Ru(001) substrate followed by 1 ML of Ag.

Figure 5 shows the high-resolution valence-band photoemission spectra for a series of Ag/Au/Ru(001) at various coverage, where Au was deposited first on a Ru(001) substrate followed by Ag. It should be noted that all Au coverage are 1 ML except in one case (66.7% Au) where 2 ML of

Au was used. For presentation purposes, each spectrum was normalized to the background signal at 9 eV binding energy. We can see from the figure that the alloy *d* bandwidth decreases significantly on going from 2 ML Au/Ru (4.26 eV) through various Au composition to 3 ML Ag/Ru (2.70 eV). The bottom of the alloy *d* band stays in place as Au becomes more dilute, whereas the top of the alloy *d* band (closer to the Fermi level) moves steadily towards a higher binding energy (2.56–4.24 eV). This phenomenon was well documented in bulk alloys<sup>10,11</sup> (see Fig. 2). A reduction in the apparent spin-orbit splitting between the “Au *d*-band” maxima can also be seen. We recall that this behavior primarily reflects changes in the Au 5*d*<sub>5/2</sub> component, which is most sensitive to chemical changes and exhibits the largest movement in the photoemission spectrum, while the other *d*-band components (Ag 4*d*<sub>5/2,3/2</sub> and Au 5*d*<sub>3/2</sub>) do not. This *d*-band behavior is inevitably accompanied by a shift of the centroid of the *d* band away from the Fermi level from 4.18 eV in a concentrated Au system (Ag/Au/Ru) to 5.36 eV in a dilute Au system (8 Ag/Au/Ru). Note that the centroid positions for Au/Ru, 2 Au/Ru are 4.31 and 4.25 eV, respectively.<sup>15</sup> These observations, together with the movement of the top of the *d* band, indicate intermixing/alloying upon deposition for the more dilute Au concentrations (Au < 50%).

After annealing at 600 K, there are no significant differences in the valence-band spectra between the as-deposited and the annealed systems except for 8Ag/Au/Ru. Figure 6 compares the valence-band spectra of the most concentrated and the most dilute Au system in this study, the as-deposited and annealed Ag/2Au/Ru and 8Ag/Au/Ru system, respectively, before and after annealing. It can be seen that while the concentrated sample changes little, two noticeable changes occur for the dilute sample upon annealing. First, the intensity of the “Au *d*-band” component increases (see double-sided arrow in Fig. 6) and the Ru signal becomes slightly more noticeable (downward arrow in Fig. 6). The increase in the Au signal means that Au has migrated from the interface into the Ag layer towards the surface. The presence of a slightly noticeable Ru substrate signal (see arrow) indicates a small degree of 3D island formation resulting in the exposure of some underlying Ru(001) surface. It is also interesting to note that no further reduction in the overall *d* bandwidth takes place upon annealing. The large reduction in overall *d* bandwidth and apparent spin-orbit splitting of the “Au *d*-band” component, as well as the shift of the centroid, which occur at room temperature, indicate that alloy formation readily occurs upon deposition. The top of the alloy *d* band (3.12 eV) for 8Ag/Au/Ru, for example, is significantly tighter bound than that of the 1 ML Au/Ru (2.8 eV).

Alloying is also evident from the core-level shifts of Au and Ag relative to the pure metal (1 ML Au/Ru). Table I shows the Au 4*f* core-level parameters obtained at 170 eV photon energy for the Ag/Au/Ru systems. All shifts are relative to 1 ML Au/Ru. A shift towards higher binding energy is evident except for the concentrated Au sample (Ag/2Au/Ru). This observation is consistent with the 1.5 ML Au/Ru results reported previously.<sup>15</sup> The Au 4*f*<sub>7/2</sub> surface component for the 1.5 ML Au/Ru coverage is located at 83.66 eV. If the core-level position for the Ag/2Au/Ru was referenced to the position of 1.5 or 2 ML Au/Ru, a positive binding-

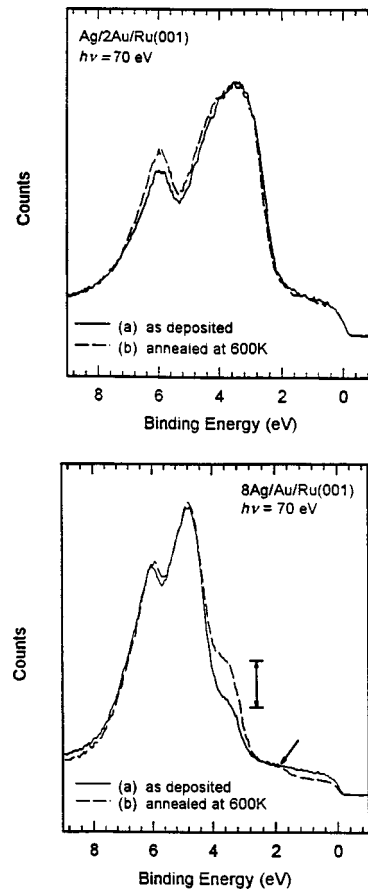


FIG. 6. Upper panel: Valence-band spectra for Ag(1 ML)/Au(2 ML)/Ru: (a) as-deposited, (b) annealed at 600 K for 5 min. Lower panel: Valence-band spectra for Ag(8 ML)/Au(1 ML)/Ru: (a) as-deposited, (b) annealed at 600 K for 5 min.

energy shift of 0.06 eV would result. The rest of the data exhibits a steady shift away from the Fermi level and stays the same (within experimental error) after annealing. This observation suggests that the 2D alloy between Au and Ag forms at room temperature upon deposition for the two dilute systems (Au < 50%), 3Ag/Au/Ru and 8Ag/Au/Ru.

The Ag 3*d* XPS core-level parameters for the Ag/Au/Ru system [Table I(b)] show a small shift towards lower binding energy for all of the spectra except for the 3Ag/Au/Ru, which exhibits a 0.06 eV shift that reduces to 0.04 eV upon annealing. These values are only qualitative due to the limited resolution of the conventional x-ray source. Notice that all of the data in Table I(b) are compared to the 1 ML Ag/Ru and that the 3*d* core level for 3 ML Ag/Ru is located at 368.13 eV. If we compared the 3Ag/Au/Ru system to 3Ag/Ru, the resulting shifts would be both negative. The results for the dilute Ag system Ag/2.5Au/Ru and Ag/3Au/Ru are statistically significant. These shifts indicate alloy formation, in good agreement with the bulk Au results. It can be seen from Table I(b) that the intensity of the Ag 3*d* are of some interest. It decreases following annealing for all of the coverage, indicating further intermixing upon annealing. The peak intensity change varies from ~1% for the dilute (3Ag/Au/Ru) to 10% for the concentrated Au coverage (Ag/3Au/Ru). These results suggest that there is little alloying when 1 ML of Au is deposited first (supporting the Au results) but



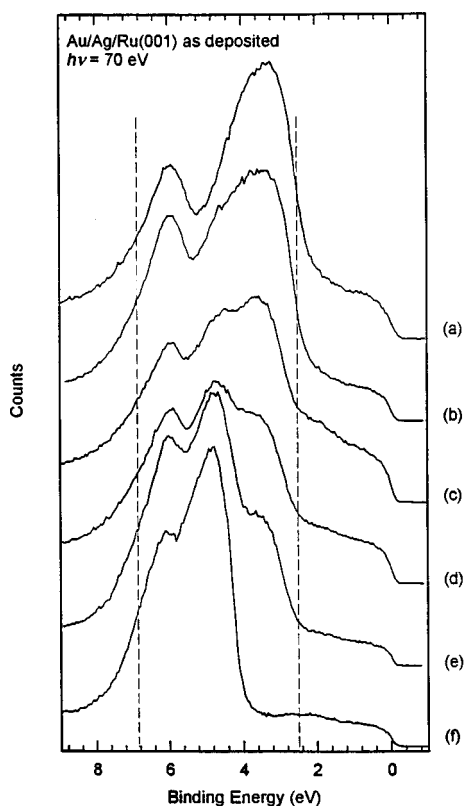


FIG. 7. Valence-band spectra for the Ag first, as-deposited Au/Ag/Ru system: (a) Au(2 ML)/Ru, (b) Au(2 ML)/Ag(1 ML)/Ru, (c) Au(1 ML)/Ag(1 ML)/Ru, (d) Au(1 ML)/Ag(2 ML)/Ru, (e) Au(1 ML)/Ag(8 ML)/Ru, and (f) Ag(3 ML)/Ru. The vertical lines mark the top and the bottom of the  $d$  band.

substantial alloying when more than 1 ML of Au is deposited first. This suggests that Au above the first layer are more reactive towards alloying.

### C. Au/Ag/Ru(001) multilayers with Ag deposited first

Figure 7 is the valence-band photoemission spectra for the as-deposited multilayer Au/Ag/Ru(001). Spectra for 2 ML Au/Ru and 3 ML Ag/Ru are also shown in Figs. 7(a) and 7(f), respectively, for comparison. The vertical lines indicate the positions of the top and bottom of the 2 ML Au/Ru  $d$  band [Fig. 7(a)]. The graph is dominated by the Au  $d$ -band components at high Au concentrations and by the Ag  $d$ -band components at low Au concentrations. A substantial narrowing of the overall  $d$  band takes place on going from concentrated [2Au/Ag/Ru, Fig. 8(b)] to dilute [Au/8Ag/Ru, Fig. 8(e)] Au/Ag/Ru adlayers. It is the top of the  $d$  band (mostly Au  $5d_{5/2}$  character) that moves away from the Fermi level, resulting in the narrowing of the overall band, whereas the bottom of the  $d$  band retains its original position. This behavior has been seen in the bulk alloys and indicates that the edge closest to the Fermi level is most sensitive to chemical changes. The apparent spin-orbit doublet separation of the “Au  $d$  band” also reduces on going from high coverage (2.43 eV) to dilute coverage (2.28 eV). The  $d$ -band centroid moves from 4.46 eV for the 2Au/Ag/Ru to 5.09 eV for the Au/8Ag/Ru sample. The Au/Ag/Ru system after annealing at 600 K for 5 min exhibits only a small narrowing in the

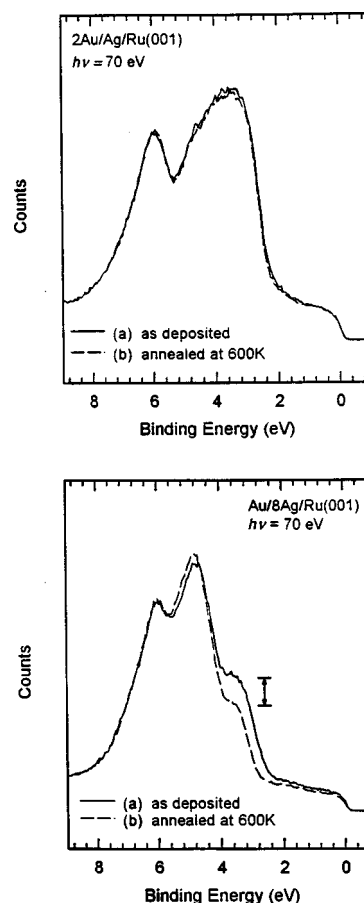


FIG. 8. Valence-band spectra for the Au(2 ML)/Ag(1 ML)/Ru (upper panel) and Au(1 ML)/Ag(8 ML)/Ru (lower panel) before and after annealing at 600 K for 5 min.

$d$ -band width for the dilute samples ( $\sim 0.1$  and  $0.2$  eV for Au/2Ag/Ru and Au/8Ag/Ru, respectively). This is accompanied by the movement of the top of the  $d$  band away from  $E_F$ . The centroid position, however, changes substantially only for the Au/8Ag/Ru sample (5.09–5.21 eV). The apparent spin-orbit splitting of the “Au  $d$ -band” components follows the same trend as the  $d$ -band width.

Figure 8 compares the most concentrated [2Au/Ag/Ru in Fig. 8(a)], and the most dilute [Au/8Ag/Ru in Fig. 8(b)] sample of the series, prior to and after annealing at 600 K for 5 min. For the 2Au/Ag/Ru sample, no change can be seen after annealing other than a barely noticeable narrowing of the overall  $d$  band. Since annealing has little effect on the sample it is possible that this sample either forms an alloy readily at room temperature upon deposition or does not alloy at all even at elevated temperatures. This cannot be decided on  $d$ -band width alone, since the alloy  $d$  band is less sensitive to alloying for Au rich alloys (Au > 50%). However, in the Au/8Ag/Ru system, the  $d$  band narrows noticeably (especially the position of the top of the  $d$  band) relative to Au/Ru even before annealing and narrows further after annealing. The overall  $d$  band narrows by 0.21 eV and the centroid shifts to a higher binding energy from 5.09 to 5.21 eV. Furthermore, the intensity of the “Au  $d$ -band  $5/2$ ” component decreases. This indicates that Au atoms sink further into the Ag layers underneath upon annealing. This behavior is the reverse of what has been seen in Fig. 3 for the 8Ag/

Au/Ru sample, where Au moves towards the surface. A comparison of the spectra reveals that after annealing, Au/8Ag/Ru and 8Ag/Au/Ru exhibit identical valence-band spectra.

The Au 4*f* core-level parameters at 170 eV for the as-deposited and annealed Au/Ag/Ru system are given in Table II(a). All changes are compared to the 1 ML Au/Ru sample. It appears that the 2Au/Ag/Ru core level is shifted to a lower binding energy with respect to the 1 ML Au/Ru peak. However, a shift to a higher binding energy is seen if the data is compared with a 2-ML Au/Ru sample. This behavior was also observed in the previous section and is not surprising since the data for the 2Au/Ag/Ru system should be compared to that of 2 ML Au/Ru. The Au *f* core levels for the remaining coverage, which all contain 1-ML Au layer and 1 or more ML Ag, are compared to the 1 ML Au/Ru. Surprisingly, these systems exhibit a constant shift to higher binding energies in spite of decreasing Au concentration in the overlayers. However these shifts increase noticeably after annealing. This suggests that at compositions of Au  $\leq$  50%, an alloy with a constant composition (most likely 50-50, see below) is formed upon deposition. Annealing, however, promotes further intermixing, which results in the formation of a stable stoichiometric Au-Ag alloy on Ru.

The results of Ag 3*d* core levels obtained with conventional XPS for the as-deposited Au/Ag/Ru(001) system are presented in Table II(b). Peak areas are shown in parentheses. Notice that the Au/3Ag/Ru exhibits a positive shift when compared with 1 ML Ag/Ru. When compared with 3 ML Ag/Ru(001) (*B.E.* = 368.13), the core-level shift for the Au/3Ag/Ru system is  $-0.07$  and  $-0.06$  eV prior to and after annealing at 700 K, respectively. Similar negative shift was also seen for the reverse deposition discussed in the previous section. The remaining systems also exhibit negative Ag core-level shifts, a sign of alloying as observed in bulk alloys. For the Au/3Ag/Ru sample the peak areas increase by 16.5% upon annealing. This suggests that annealing promotes complete intermixing in this system.

#### D. Effect of order of deposition and annealing on surface alloy formation

From the above-reported bilayer and multilayer Ag/Au/Ru(001) and Au/Ag/Ru(001) results, we can now examine the effect of the order of deposition and annealing on the interaction between the coadsorbates and between the adsorbate and the Ru substrate. A number of trends can be established by correlating the following sets of parameters: overall *d*-band width, centroid of the *d* band, apparent spin-orbit splitting of the Au 5*d* components, Au 4*f* shifts, and Ag 3*d* shifts, with the composition of the overlayers. These correlations will be used to infer surface alloying.

Figure 9 shows the width of the overall alloy *d* band. The top and bottom graphs depict the overall *d*-band-width as a function of the overlayer composition for the Au first, Ag/Au/Ru(001) and Ag first, Au/Ag/Ru(001) systems, respectively. It must be noted that the composition is based mostly on 1 ML of Au and several monolayers of Ag. The 4.25 eV for the 100% Au is based on 2Au/Ru (the *d*-band-width varies from 4.1 eV for Au/Ru to 4.4 eV for 3Au/Ru in our measurements<sup>15</sup>). We selected 1-ML Au coverage because

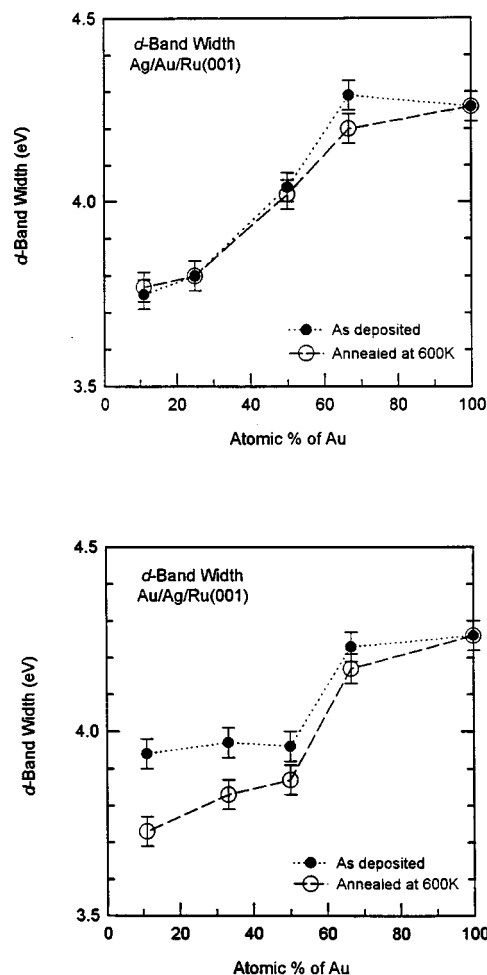


FIG. 9. A plot of *d*-band width versus overlayer composition for Ag/Au/Ru (top) and Au/Ag/Ru (bottom) systems.

the influence of Ru on the adlayer is the strongest at 1 ML. Since all the adsorbed Au are in contact with Ru, once the layer becomes thicker the substrate influence will be reduced significantly. A decrease in bandwidth is seen for the Ag/Au/Ru system as the Au concentration decreases. This trend does not change after annealing (except for samples where Au is more than 2 ML). This suggests that alloying takes place at room temperature for compositions of Au  $<$  50%. After annealing, however, alloy is formed for Ag/2Au/Ru. The 50-50 composition, as discussed above, maintains a width comparable to that of Au/Ru (4.1 eV) and does not form alloy.

The Au/Ag/Ru system, seen at the bottom of Fig. 9, exhibits a noticeably different behavior. The overall *d* band narrows slightly for the 2Au/Ag/Ru coverage, (0.03 eV) with respect to 2Au/Ru(001). The width decreases noticeably for the Au/Ag/Ru(001) sample (0.27 eV relative to 2Au/Ru, 0.11 eV relative to Au/Ru). As noted earlier, the bandwidth remains virtually the same for coverage with Au concentration  $\leq$  50 at. %. This indicates that a stable (50/50) Au-Ag alloy is formed at the surface of the Ag overlayers. It is interesting to note that for ideal mixing, the  $\Delta G$ , Gibb's free energy of mixing is a minimum at 50-50 composition. Further increase in the thickness of the underlying Ag layer has no effect on the composition of the alloy formed under as-deposited con-

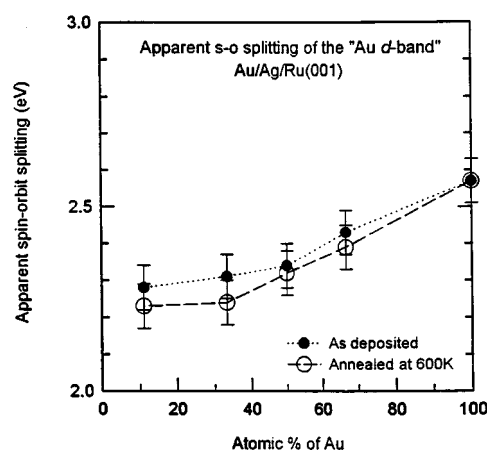
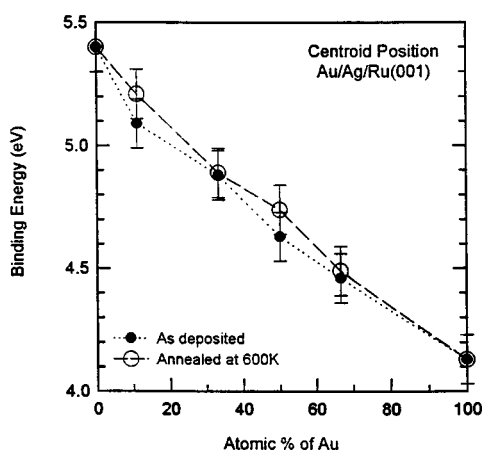
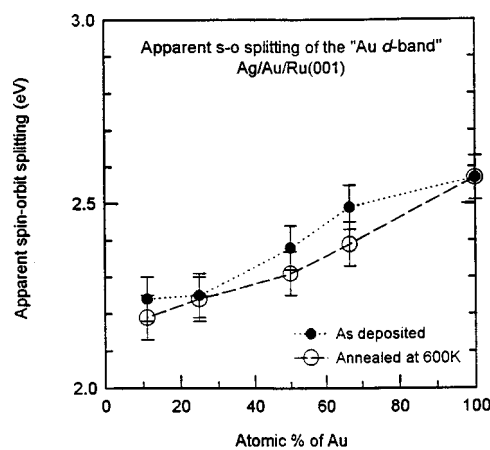
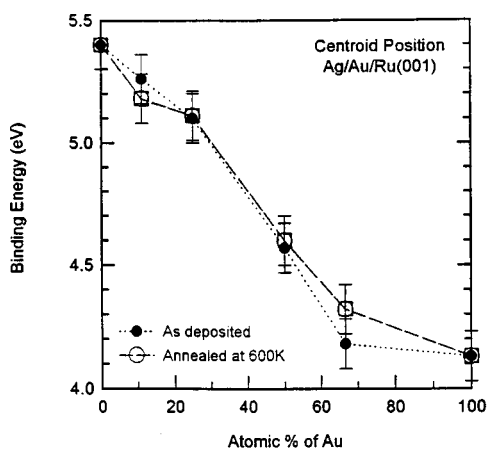


FIG. 10. Plot of  $d$ -band centroid position versus overlayer composition for Ag/Au/Ru (top) and Au/Ag/Ru (bottom) systems.

ditions. However, the bandwidth narrows further upon annealing to 600 K when the trend seen for the Ag/Au/Ru system is observed for the Au/Ag/Ru samples (bottom of Fig. 9). This result suggests that further intermixing takes place at elevated temperatures resulting in the formation of stoichiometric alloys. Thus, the order of deposition and annealing temperature both play a crucial role in two-dimensional Au-Ag alloy formation on a Ru(001) surface. It is almost certainly that the Ru substrate modifies alloy formation most significantly in the 1-ML regime (i.e., 1 ML Au and 1 ML Ag) in that it keeps the adlayer two-dimensional, and this becomes less important at increased coverages<sup>22</sup> where mass action takes its normal course.

We now examine the overall  $d$ -band centroid position as a function of the deposition order and annealing temperature. These parameters should establish a correlation consistent with that of the alloy  $d$ -band-width. Figure 10 presents a correlation of the centroid position for the Ag/Au/Ru and Au/Ag/Ru systems in the top and bottom panels, respectively. We recall that the overall  $d$ -band centroid position is influenced by several factors: variations in cross sections of the Au and Ag components, changes in the Au and Ag  $d$ -band contributions (composition), and shifts due to alloying. We have studied the variation of cross section at photon energies from 50 to 100 eV and found that there is no anomaly in the cross section within this energy range, and

FIG. 11. Plot of apparent spin-orbit splitting of the Au  $d$  band versus overlayer composition for Ag/Au/Ru (top) and Au/Ag/Ru (bottom) systems.

that 70 eV photon energy appears to be a desirable energy for studying the alloys in terms of energy resolution, photon flux, and relative cross section. The effect of composition is more difficult to deal with. In general, the more dilute Au is the more Ag like the  $d$  band is. It is, therefore, not surprising from Fig. 10 that the correlation follows the general trend observed for bulk alloys (i.e., a shift to a higher binding energy when Au is diluted in Ag). Since the centroid shift is largely determined by the movement of the Au  $d$  band, which is partially buried under the Ag  $d$  band and broadens as the result of Ag-Au  $d$ - $d$  interaction, its use as a monitor is at best semiquantitative.

A comparison of the apparent spin-orbit splitting between the "Au  $d$ -band" maxima in Ag/Au/Ru and Au/Ag/Ru samples is presented in the top and bottom panel of Fig. 11, respectively. It should be emphasized that the positions of the "Au  $d$ -band" components were obtained by removing the underlying Ag and Ru signals. Since the Au " $5d_{3/2}$ " component overlaps with the Ag " $4d_{5/2}$ " and we assume that alloying does not alter the position of the Ag  $d$ -band and the Au  $d_{3/2}$  component greatly, these estimates will have large uncertainty and are at best qualitative. The reduction in the apparent spin-orbit splitting of Au on going from concentrated to dilute Au-Ag overlayer is evident from Fig. 11. One may argue that a plateau (for a surface 50/50 alloy), similar

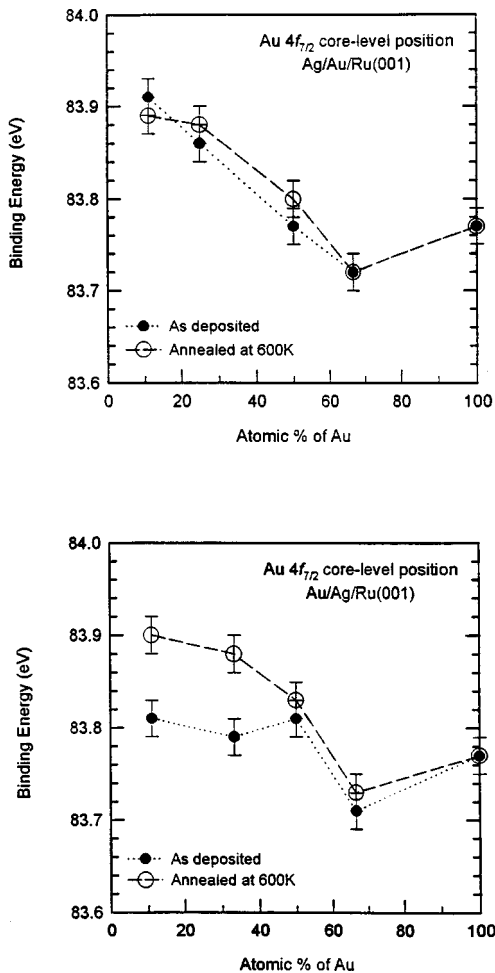


FIG. 12. Plot of Au  $4f_{7/2}$  binding energy versus overlayer composition for Ag/Au/Ru (top) and Au/Ag/Ru (bottom) systems.

to the one seen in the bandwidth analysis, is seen in the bottom panel for the as-deposited sample. The apparent spin-orbit splitting trends indicate that the Au  $5d$  levels are tighter bound in the alloy. This behavior is expected for Au alloys in general.

Figure 12 compares the Au  $4f_{7/2}$  core-level binding energy shifts in Ag/Au/Ru (top panel) and Au/Ag/Ru (bottom panel) before and after annealing. All core-level positions are referenced to the Fermi level and are compared to a 1-ML Au/Ru sample [Table I(a)]. It follows that 100% Au in these plots does not refer to bulk Au binding energy (83.92 eV). Also the Ag/2Au/Ru should be compared with 2Au/Ru (83.66 eV) as noted earlier. For the Ag/Au/Ru system the Au  $4f$  core level of the dilute systems ( $Au < 50\%$ ) shifts away from the Fermi level for the as-deposited sample relative to Au/Ru and stays unchanged after annealing to 600 K. This observation is consistent with the bandwidth trend and suggests that alloying readily takes place at room temperature when Au is deposited first on a Ru(001) substrate followed by more than 1 ML of Ag.

The bottom panel of Fig. 12 reveals a different behavior when the order of deposition is reversed. For the as-deposited samples, the Au  $4f$  core levels shift to about 83.8 eV for the Au/Ag/Ru overlayers and remain there despite further increase in the thickness of the Ag adlayer. This suggests that a 50/50 Au-Ag alloy forms at the interface between

the Au and Ag adlayers and its composition remains the same even if the amount of Ag is increased. After annealing, however, the trend for Au/Ag/Ru is similar to what is observed in the top panel for the Ag/Au/Ru series. This indicates that stoichiometric alloy formation takes place only at elevated temperatures. The Au  $4f$  core-level shifts, therefore, confirm the formation of a 50/50 surface alloy in the Au/Ag/Ru system upon deposition. Trends from Ag  $3d_{5/2}$  core-level shifts [Tables I(b) and II(b)] are less revealing due to a limited experimental energy resolution. They do exhibit a trend qualitatively parallel to that of bulk alloys, however.

From all of the above trends, it is clear that the order of deposition has an effect on the degree of intermixing and alloy formation. When 1 ML of Au is deposited first, followed by several layers of Ag a stoichiometric surface alloy is formed at room temperature. For the reversed order of deposition (i.e., 1 to several ML of Ag deposited first), a 50/50 Au-Ag/Ru alloy forms at the surface of the Ag overlayers at room temperature. Annealing promotes further intermixing, which results in the formation of stoichiometric Au-Ag alloy. The Ru(001) substrate appears to play a crucial role at 1-ML coverage of Au and Ag (i.e., 1 ML Au and 1 ML Ag on Ru) and its effect diminishes greatly when the overlayer atoms are no longer in contact with the Ru substrate. This is also borne out in TDS studies where the first monolayer always desorbs at higher temperature than the second and the multilayers. However, the second layer is still perturbed by the presence of the Ru(001) substrate. The effect of adsorbate-substrate interaction on alloying (for layer-by-layer and SK growth modes at least) may be generalized as: monolayer (strongly affected), second layer (weakly affected), and multilayer (little).

### E. Comparison of surface and bulk alloying

Two noticeable differences between Au-Ag two-dimensional alloying on Ru(001) and bulk alloying are the temperature factor and the use of the physical vaporization deposition (PVD) process. In bulk alloys, stoichiometric amounts of the alloy constituents have to be melted at high temperatures in order to form an alloy.<sup>26</sup> In contrast to bulk events, it has been shown that surface alloying on Ru(001) can take place at room temperature and perhaps at lower temperatures. The PVD process clearly reduces the energetics requirement for alloying. This effect has been observed for Au-Cu surface alloys on Ru(001) where alloying occurs at room temperature (we are referring to the substrate temperature during deposition) regardless of the deposition order.<sup>27,28</sup> In addition, surface alloys will inevitably have more atoms in the surface and in the interface between the overlayers and the substrate. Thus, the average co-ordination number of nearest like atoms is expected to decrease relative to that of the bulk. In order to investigate whether or not there is any observable difference in the electronic structure between the 2D surface and bulk Au-Ag alloys with the same stoichiometry, we compare below the valence-band behavior and core-level shifts between the two systems.

Figure 13 presents a comparison between the alloy  $d$ -band parameters (bandwidth, centroid, and apparent spin-orbit splitting) in bulk and surface alloys recorded under similar experimental conditions. It can be seen that the overall alloy bandwidth narrows in both systems from high at. % of Au to

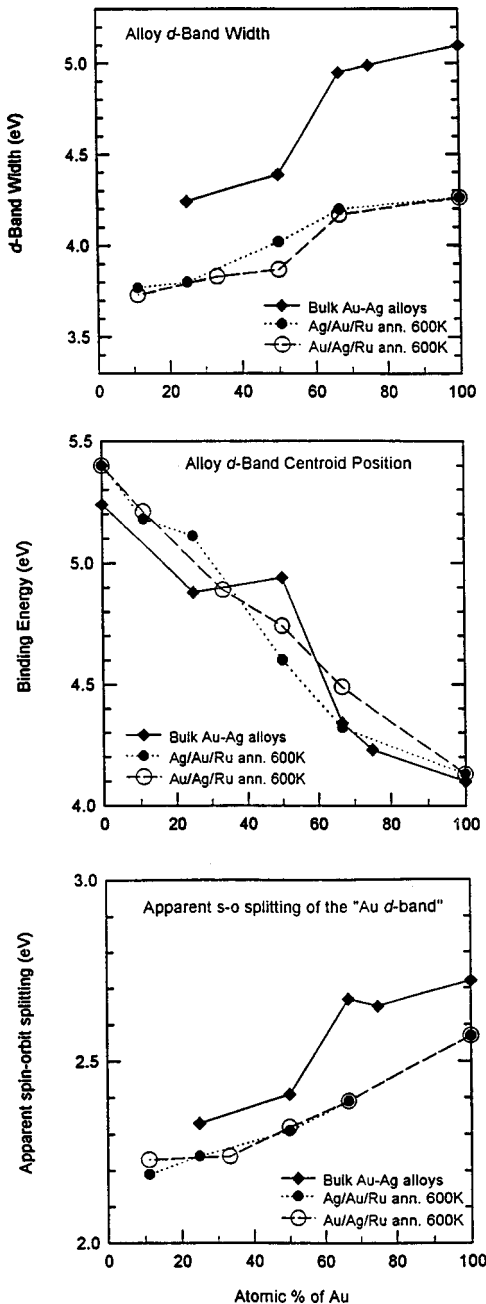


FIG. 13. Comparison of  $d$ -band parameters versus composition between bulk and surface alloys; from top to bottom:  $d$ -band-width, centroid position, and apparent spin-orbit splitting.

dilute Au alloys. The  $d$  bands of the bulk Au-Ag alloys are  $\sim 0.5$  eV wider than those of the surface alloys. This can be understood on the basis of the co-ordination number of like nearest neighbors. The greater the number of like nearest neighbors the wider the band. For example, in a closest packed surface [fcc(111) or hcp(001)], the coordination number of the surface atom is reduced from 12 to 9. For systems with strong  $d$ - $d$  interaction, the bandwidth [the  $\Delta_{\text{band}}$  term discussed above in Eq. (1)] can be scaled to  $N^{1/2}$  where  $N$  is the coordination number of nearest like atoms.<sup>30,31</sup> This would lead to a  $\sim 15\%$  reduction in the band term. The actual observed width would be considerably smaller after the spin-orbit (atomic term) and experimental resolution were accounted for. This is because the alloy  $d$

band has both Ag and Au contributions, and only the upper  $d$  band of Au character is largely responsible for the bandwidth changes. For surface alloys, the number of nearest neighbors is reduced at the surface and the interface (which contributes less to the signal due to the short electron escape depth at our experimental energies), because of the two-dimensional nature of the alloys. Consequently, the width of the overall  $d$  band of a surface alloy is narrower than that in the bulk alloy of the same stoichiometry. A reduction of  $<15\%$  would be expected for surface alloys. The observed reduction is  $\sim 10\%$  for dilute surface Au alloys, in good qualitative agreement with the estimate.

A comparison between the position of the  $d$ -band centroid in bulk and surface alloys is shown in Fig. 13(b). They exhibit the same trend as the  $d$ -band-width as expected because the narrower the  $b$  band the farther away the centroid from the Fermi level, since the Au " $d_{5/2}$ " component always moves away from the Fermi level in Au alloys. It can be seen that except for a deviation in the 50-50 bulk alloy, there is indeed a shift of the centroid away from the Fermi level for both the surface and the bulk alloys upon dilution of Au in Ag.

The apparent spin-orbit splitting of the "Au  $d$ -band" maxima in bulk and surface alloys are compared in Fig. 13(c). Here, once again we focus on the Au  $d$  components because the Au  $d_{5/2}$  component is most conspicuous and most chemically sensitive. It can be seen that the separation of the doublet components becomes smaller from concentrated to dilute Au-Ag alloys for both systems as expected. The splitting for bulk alloys, is slightly larger (0.1 eV) than that for the surface alloys. Again, this difference can be explained in terms of the number of nearest-neighboring like atoms, which also determines the overall  $d$ -band-width. It is important to emphasize again that the "Au component" of the alloy  $d$  band is very sensitive to alloying. Because of the direct overlap in binding energy between part of the Au and Ag  $d$  bands, it has been conventionally assumed that for 50% or higher Au concentration, Au and Ag  $d$  bands intermix substantially and may lose their individual character.<sup>6</sup> The high-resolution results reveal that the Au component of the  $d$  band retains considerable Au character after alloying, even at concentrations greater than 50%. Finally, both surface overlayer systems (i.e., Ag/Au/Ru and Au/Ag/Ru) with the same composition and coverage show similar apparent spin-orbit values after annealing. This indicates that at elevated temperatures ( $>600$  K) both systems form alloys whose composition is determined by the stoichiometric proportions of Au and Ag except in the case of Ag/Au/Ru (1 ML each, see Sec. III A).

Figure 14 compares Au  $4f_{7/2}$  shifts between bulk and surface alloys. The Au  $4f$  shifts to higher binding energy for both alloy systems as the Au concentration decreases. The position of the Au  $4f_{7/2}$  core level in bulk alloys is, however, about 0.15-eV higher in binding energy than in surface alloys. This stems from the difference in binding energy between the surface and bulk atoms. It has been shown<sup>22,29</sup> that the Au  $4f$  core level for the surface Au atoms of a Au metal is at 83.61 eV, and that for Au atoms inside the bulk Au sample is at 84.01 eV. This difference in binding energy has been attributed to different co-ordination number of nearest like-atoms (Au) at the surface versus the bulk. A reduction in

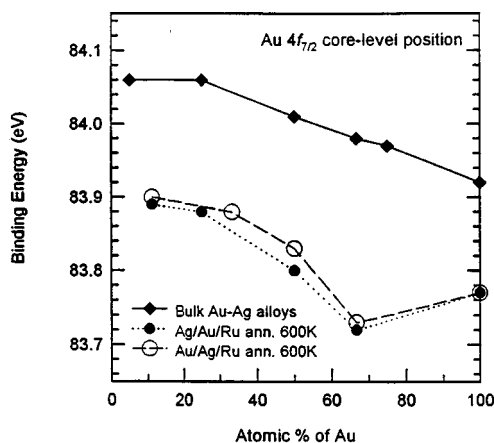


FIG. 14. Comparison of Au  $4f_{7/2}$  binding energy of the Au  $d$  band in bulk and surface alloys.

coordination number narrows the *surface d* band and the alignment of the surface and bulk Fermi levels produces a negative binding-energy shift for the surface atoms of the metals with the  $d$  band more than half-filled.<sup>29</sup> This interpretation applies to both bulk and surface alloys. By using the same argument, the offset ( $\sim 0.15$ -eV lower in binding energy for surface alloys) can be explained by the fact that in these thin alloys, due to the presence of the surface and the interface, the average coordination number for nearest Au atoms is significantly smaller than those in bulk alloys. The Au  $d$ - $d$  interaction is not as extensive in surface alloys because of the reduction in coordination number of like neighbors and the truncation of the lattice. The net result is a narrower surface  $d$  band and a  $4f$  shift to lower binding energy.<sup>29</sup> Moreover, interaction of the adsorbate with the Ru substrate also contributes to keeping the alloy two-dimensional (reducing the Au-Au interaction). The two surface systems exhibit a similar trend after annealing. This supports previous conclusions on the degree of alloying and importance of annealing to surface alloy formation in the Au/Ag/Ru system.

The Ag  $3d_{5/2}$  core-level shifts between surface and bulk alloys reveal an opposite trend to the Au  $4f$  shifts: that is that relative to pure Ag, there is a shift towards the Fermi

level for Ag in both surface and bulk alloys upon dilution of Ag in Au. However, the Ag  $3d_{5/2}$  core-level shifts have larger uncertainties due to a smaller shift, limited energy resolution, and a larger core lifetime broadening. The general Ag  $3d$  trend suggests that alloying takes place on the surface of a Ru(001) crystal but is not sensitive enough to distinguish between the surface and the bulk alloys.

#### IV. CONCLUSIONS

We have presented a study of two-dimensional alloying between Au and Ag overlayers adsorbed on a Ru(001) surface using primarily a 1-ML Au/Ru system. We have shown with photoemission results that for one monolayer each of Ag and Au adsorbed on Ru(001) alloying occurs when Ag is deposited first. No evidence of alloying is found for the reversed order of deposition [Ag/Au/Ru(001)]. These results have been attributed to strong Au-Au and Au-Ru interactions relative to that of Ag-Au and Ag-Ru in the monolayer regime, as was also shown in TDS experiments.

For a series of multilayer Ag/Au/Ru(001) systems (Au deposited first) with coverage  $\geq 1$  ML for both metals, the valence-band and core-level photoemission at various coverage were studied. The result suggest that for Ag coverage greater than 1 ML, alloying occurs readily at room temperature both at low and high Au concentrations. The composition of the two-dimensional alloys formed reflects the stoichiometric ratios of the constituents deposited onto Ru.

The results for the Au/Ag/Ru system, where Ag was deposited first, suggest that for overlayers containing  $\leq 50$  at. % Au (Au/ $n$ Ag/Ru where  $n > 1$ ), a stable 50/50 Au-Ag surface alloy, not a stoichiometric one, is formed upon deposition at room temperature. Stoichiometric surface alloys are formed only at elevated temperatures. By comparing the photoemission valence-band and core-level shifts for bulk and surface alloys of the same stoichiometry, we find that the surface alloy  $d$  band is slightly narrower than that of the bulk. This observation is attributed to the two-dimensional nature of the surface alloy (lower coordination number of like atoms). A  $\sim -0.15$  eV shift in the binding energy of the Au  $4f$  core levels in surface alloys relative to that of the bulk alloys has been observed and is attributed to the same effect.

\*Present address: Scalac Inc., 155 Hachborn Rd., Unit 3, Brantford, ON, Canada N3T 5M1.

†Present address: Intel Massachusetts Inc., 75 Reed Rd. HD1/G1, Hudson, MA 01749-2895.

<sup>1</sup>J. Friedel, *Philos. Mag.* **43**, 153 (1952).

<sup>2</sup>I. M. Templeton and P. T. Coleridge, in *Proceedings of the 14th International Conference on Low Temperature Physics*, edited by M. Krusius and M. Vuotio (North-Holland, Amsterdam, 1975), p. 143.

<sup>3</sup>P. H. Barrett, R. W. Grant, M. Kaplan, and D. A. Shirley, *J. Chem. Phys.* **39**, 1035 (1963).

<sup>4</sup>L. D. Roberts, R. L. Becker, F. E. Obenshain, and J. O. Thomson, *Phys. Rev.* **137**, A895 (1965).

<sup>5</sup>R. E. Watson, J. Hudis, and M. L. Perlman, *Phys. Rev. B* **4**, 4139 (1971).

<sup>6</sup>G. K. Wertheim, L. F. Mattheiss, and D. N. E. Buchanan, *Phys. Rev. B* **38**, 5988 (1988).

<sup>7</sup>J. W. Niemantsverdriet, P. Dolle, K. Markert, and K. Wandelt, *J.*

*Vac. Sci. Technol. A* **5**, 875 (1987).

<sup>8</sup>K. Wandelt, J. W. Niemantsverdriet, P. Dolle, K. Markert, and K. Wandelt, *J. Vac. Sci. Technol. A* **5**, 875 (1987).

<sup>9</sup>K. Markert, P. Dolle, J. W. Niemantsverdriet, and K. Wandelt, *J. Vac. Sci. Technol. A* **6**, 1752 (1988).

<sup>10</sup>T. K. Sham, A. Bzowski, M. Kuhn, and C. C. Tyson, *Solid State Commun.* **80**, 29 (1991).

<sup>11</sup>C. C. Tyson, A. Bzowski, P. Kristof, M. Kuhn, R. Sammynaiken, and T. K. Sham, *Phys. Rev. B* **45**, 8924 (1992).

<sup>12</sup>Z. W. Lu, S.-H. Wei, and A. Zunger, *Phys. Rev. B* **44**, 10 470 (1991); A. Zunger, S. H. Wei, L. G. Ferreira, and J. E. Bernard, *Phys. Rev. Lett.* **65**, 353 (1990).

<sup>13</sup>J. A. Rodriguez, *Surf. Sci.* **296**, 149 (1993).

<sup>14</sup>A. Bzowski, M. Kuhn, T. K. Sham, and K. H. Tan, *J. Vac. Sci. Technol. A* **12**, 1790 (1994).

<sup>15</sup>A. Bzowski, T. K. Sham, M. Werneirt, and R. E. Watson, *Phys. Rev. B* **51**, 9979 (1995).

- <sup>16</sup>R. Q. Hwang, J. Schroder, C. Gunther, and R. J. Behm, Phys. Rev. Lett. **67**, 3279 (1991).
- <sup>17</sup>R. M. Friedman, J. Hudis, M. L. Perlman, and R. E. Watson, Phys. Rev. B **8**, 2433 (1973).
- <sup>18</sup>T. K. Sham, M. L. Perlman, and R. E. Watson, Phys. Rev. B **19**, 539 (1979).
- <sup>19</sup>A. Bzowski, T. K. Sham, and Y. M. Yiu, Phys. Rev. B **49**, 13 776 (1994)
- <sup>20</sup>A. Bzowski, Y. M. Yiu, and T. K. Sham, Jpn. J. Appl. Phys., Suppl. **32-2**, 691 (1993).
- <sup>21</sup>W. Drube, R. Treusch, T. K. Sham, A. Bzowski, and A. V. Soldatov, Phys. Rev. B **58**, 6871 (1998).
- <sup>22</sup>M. Kuhn, A. Bzowski, T. K. Sham, J. A. Rodriguez, and J. Hrbek, Surf. Sci. Lett. **283**, 209 (1996).
- <sup>23</sup>J. A. Rodriguez, J. Hrbek, Y.-W. Yang, M. Kuhn, and T. K. Sham, Surf. Sci. **293**, 260 (1993).
- <sup>24</sup>J. A. Rodriguez, J. Hrbek, M. Kuhn, and T. K. Sham, J. Vac. Sci. Technol. A **11**, 2029 (1993).
- <sup>25</sup>Strictly speaking, the  $j$  values are not good quantum numbers since the magnitude of the spin-orbit interaction is comparable to band formation. They are used as notations to denote the spin-orbit origin of the splitting.
- <sup>26</sup>See, for example, W. B. Pearson, *A Handbook of Lattice Spacing and Structures of Metals and Alloys* (Pergamon, London, 1956).
- <sup>27</sup>M. Kuhn, Z. H. Lu, and T. K. Sham, Phys. Rev. B **45**, 3703 (1992).
- <sup>28</sup>M. Kuhn, J. A. Rodriguez, J. Hrbek, A. Bzowski, and T. K. Sham, Thin Solid Films **283**, 209 (1996).
- <sup>29</sup>P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. B **27**, 3160 (1983).
- <sup>30</sup>F. Cyrot-Lackmann, Adv. Phys. **16**, 393 (1967).
- <sup>31</sup>M. Kuhn and T. K. Sham Phys. Rev. B **49**, 1647 (1994).