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Photoemission study of Au overlayers on Pd(111) and the formation of a Pd-Au(111) alloy surface

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The techniques of photoemission spectroscopy (PES), Auger spectroscopy, and low-energy electron diffraction were used to examine the interaction of Au and Pd for the following: (1) overlayers of Au on Pd(111), ranging from 0.1 to 10 monolayers, (2) Au diffused into the Pd matrix, and (3) a stabilized Pd-Au alloy surface, formed by diffusing a thick Au layer into the Pd until the composition stabilized. An ordered Au(111) layer formed on the Pd. For the Au overlayers, three effects were seen by PES: (1) structures appeared which merged smoothly into the metallic Au structure, (2) structures at the energies of the clean Pd peaks were sharpened when submonolayers of Au were evaporated, and (3) a new structure appeared which could not be definitely attributed to Pd or Au. Au diffused into the Pd evidenced a more atomiclike structure than the overlayers. The stabilized alloy, which was determined to have 30 at.% Au in the surface region, evidenced PES structure strikingly similar to the 0.3 monolayer overlayer. Direct transition effects were seen for the alloy. The Au-derived structure was found to narrow and shift to slightly lower binding energy for the alloy as compared to the 0.3 monolayer overlayer. Comparison is made between the thin layers of Au on Pd and thin layers of Cu on Zn. Comparison is also made between the stabilized Pd-Au alloy and the Cu-Ni alloy system. Theoretical support for direct transitions in alloys is cited.

I. INTRODUCTION

The electronic structure of thin metal layers has been the subject of considerable study, both experimental and theoretical. The choice of substrate and overlayer material has varied widely, for example, ranging over a wide range of valence-band-energy overlap from essentially nondegenerate [such as Cu on Zn (Ref. 1)] to larger overlap such as Cu on Ag.[2] Similarly, many studies have been made of the effects of alloying on the electronic structure of the alloy components.[3–6] There has, however, been little work done to integrate these two aspects by examining the electronic structures of the metal overlayers and substrate for (1) the pure substrate, (2) submonolayer through multimonolayer overlayers, and (3) a diffused overlayer forming a model alloy surface.

In this paper, we report such a study of the Pd-Au system. Pd-Au is an example of a metal system involving considerable valence-band overlap; it is known to form a nearly ideal, completely miscible alloy at all compositions.[7] We examine the interaction between Pd and Au over the wide spectrum of conditions described below as seen through the Pd and Au electronic structures. We evaporate Au onto a single-crystal Pd (111) substrate, beginning with coverages of less than a monolayer. We then compare these Au submonolayers with Au atoms diffused into the Pd surface region by heating. We follow the electronic structure of both the Au surface layers and the corresponding diffused Au for progressively thicker Au layers of up to ten monolayers. Finally, we form a model single-crystal Pd-Au surface which is stable to approximately 800 °C, by a large Au evaporation followed by successive anneals to 800 °C until the composition in the surface region stabilizes. In this way, we are able to see, first, the effect on the Au and Pd electronic structure as the Au-Au interactions in the Au overlayer become increasingly strong and, second, the changes that take place in the Au and Pd structure when the Au is incorporated into the three-dimensional Pd lattice rather than being an overlayer on the Pd surface. The experimental methods used are photoemission spectroscopy (PES) to determine electronic structure, PES and Auger electron spectroscopy (AES) to determine compositions, and low-energy electron diffraction (LEED) to ensure surface order.

The experimental data which we obtained was unexpected and unusual. We feel that it is of major importance to present the data, and we also point out possible directions to explore in terms of theoretical explanations for the data. But we do feel that additional detailed work of a theoretical nature is necessary in order to completely explain our experimental results.

II. EXPERIMENTAL DETAILS

The experiment was performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on one of the 4° deflected beams with a "grasshopper" monochromator.[8] This monochromator, used with a 600-lines/mm grating, made photons of continuously tunable energies between 33 and ~ 300 eV available. Adjustable entrance and exit slits on the monochromator made it possible to maximize the photon flux onto the sample while maintaining the desired resolution.

The sample chamber was an Ultek stainless-steel bell-jar system. It was equipped with a PHI double-pass cylindrical-mirror analyzer (CMA) for energy analysis of the photoemitted and Auger electrons. It also had a Varian LEED system consisting of an integral electron gun and four-grid optics. A Sloan digital thickness monitor was used to calibrate the Au evaporations. A UTI quadrupole mass spectrometer was used for residual-gas analysis, and an ion gun was used for sputter cleaning. The Pd was cleaned by successive sputter-anneal cycles; this technique has been described elsewhere.[9] Pumping to a base pressure of 2×10^{-11} Torr was achieved with cryogenic and ion pumping.

III. RESULTS

A. General considerations

The continuous tunability of the synchrotron radiation gave us a good deal of flexibility in the PES studies. Thus, we could choose those photon energies which would be most useful for us. For example, the proper choice of photon energy can aid us greatly in separating the Au and Pd d bands, as will be discussed below. While we surveyed the Pd and Pd-Au electronic structures using $33 < h\nu < 160$ eV, most of the study was done at 120 and 40.8 eV for the following reasons. $h\nu = 120$ eV was a particularly important photon energy. At this energy, the photoemitted Pd $4d$ valence electrons had a kinetic energy corresponding to their Cooper minimum[10]; a sharp minimum in the photoionization cross section which occurs at characteristic energies for different subshells of electrons in different elements. In contrast, at $h\nu = 120$ eV, the photoemitted Au $5d$ valence electrons have energies corresponding to a fairly high photoionization cross section: they pass through their Cooper minimum when the photon energy is ~ 160 eV. At $h\nu = 120$ eV, the Au $5d$ cross section is quite large relative to the Pd $4d$ cross section, so the Au valence-band structure is greatly enhanced in the PES spectra at this energy. This is extremely useful, particularly in a system such as Pd-Au, where the energy overlap of the Pd and Au valence bands is so great that it would otherwise be very difficult to unambiguously attribute changes in the valence-band structure to either Pd or Au. Unfortunately, at $h\nu = 160$ eV, corresponding to the Au $5d$ Cooper minimum, the cross sections of both the Pd *and* Au valence electrons are quite small, so we were unable to obtain useful data with preferential enhancement of the Pd valence-band structure. At 120 eV, the photoemitted valence electrons have an escape depth of approximately 5 Å,[11] corresponding to little more than one atomic layer. In comparison, the escape depth of the valence electrons at $h\nu = 40.8$ eV is probably closer to two atomic layers.

The second photon energy which was chosen to be particularly useful was $h\nu = 40.8$ eV. Data taken at this energy can be easily used to compare with any future data taken from a He-discharge-lamp light source, which has a strong line at the same energy. For $h\nu = 40.8$ eV, the photoionization cross sections of the photoemitted Pd $4d$ and Au $5d$ valence electrons are such that the Pd and Au valence bands contribute approximately equally to the alloy valence-band structure. The resolution of the 40.8 eV data is ~ 0.15 eV, as compared to ~ 0.25 eV at $h\nu = 120$ eV. And finally, direct transition effects are stronger for the electrons emitted with lower energy,[12] so direct transition structures are seen more clearly in the valence bands for $h\nu = 40.8$ eV than for $h\nu = 120$ eV. For these reasons, the majority of our PES data was taken at 40.8 and 120 eV. In addition, for the stabilized Pd-Au alloy surface, we obtained data for several additional photon energies between 33 and 160 eV.

B. Au overlayers on Pd

Figures 1(a) and 1(b) show the evolution of the PES valence-band structure for increasingly large evaporations of Au overlayers on the Pd surface, at 40.8 and 120 eV, respectively. These overlayers are compared to the clean Pd spectra. LEED data from the 10-monolayer (ML) evaporation showed a clean hexagonal (1×1) pattern, indicating that a Au(111) layer had formed.

From Fig. 1, we see that clean Pd has structures stemming from the $4d$ valence electrons at -0.4, -1.5, and -3.8 eV for $h\nu = 40.8$ eV. It is nearly featureless at $h\nu = 120$ eV, due at least partially to the low photoelectron yield and poor resolution. The thick Au overlayers show, at 40.8 eV, a flat region extending to ~2 eV below E_F, corresponding to the Au *sp* electrons. Below this appear the Au 5*d* electrons, with peaks at −2.3, −3.1, −5.8, and −6.6 eV below E_F. At $h\nu=120$ eV, the thick Au layer shows again the *sp*-derived structure below E_F and 5*d*-derived peaks at −3.5 and −5.9 eV. The Au 5*d* electrons are spin-orbit split with a splitting of ~1.5 eV for isolated Au atoms.[13] Band-structure effects cause the measured splitting to increase in metallic Au, and it appears via photoemission spectra to have a value between ~2.0 and ~2.7 eV, depending on photon energy.[14]

By studying the spectra in Fig. 1(b) at $h\nu=120$ eV the splitting of the Au-derived peaks can be determined as a function of overlayer coverage. For 0.1-ML coverage, the Au-derived structures appear at −3.8 and −5.6 eV, corresponding to a 1.8-eV splitting. It increases smoothly as the Au coverage increases, finally reaching a value of 2.4 eV for 10 ML of Au. A similar effect occurs at $h\nu=40.8$ eV, though it is not so obvious, due to fine structures which are resolved at 40.8 eV, as well as the superposition of the Pd-derived structure which was suppressed at $h\nu=120$ eV. Structures appear at −3.4 and −5.6 eV for 0.3-ML Au coverage (2.2-eV splitting), which merge smoothly into the Au structure for thick overlayers. At $h\nu=40.8$ eV, the splitting increases from 2.2 eV at 0.3 ML to 2.7 eV at 10 ML. The smooth increase in the spin-orbit splitting as the Au coverage increases indicates that the Au is more atomiclike at low coverages and approaches a metalliclike state as the Au-Au distance decreases. The smoothness of the progression of the splitting with Au coverage suggests a smooth change in average Au-Au distance with coverage, which indicates well-dispersed Au atoms rather than raft or island formation. Further indication of well-dispersed Au atoms was found in subsequent chemisorption experiments. (Oxygen coverage on Pd was suppressed by a factor of more than 5 when only 0.3 ML Au was added. Well-dispersed Au atoms are strongly indicated by the magnitude of the effect.) Though the individual Au-derived structures do shift with coverage, the Au *d* bands seem to remain centered at a fairly constant energy for all coverages, at ~−4.5 eV for $h\nu=40.8$ eV and ~−4.7 eV for $h\nu=120$ eV.

Additional effects become visible at $h\nu=40.8$ eV as the Au evaporations progress. First of all, it is apparent, especially at 0.3-ML coverage, that the structures at −0.4 and −1.5 eV, close to the energies of the structures of the clean Pd, are much stronger and sharper than for the clean Pd. This effect remains, at least for the −1.5-eV peak, for coverages as high as 1 ML Au. One surprising aspect is that these sharpened structures appear above the Au

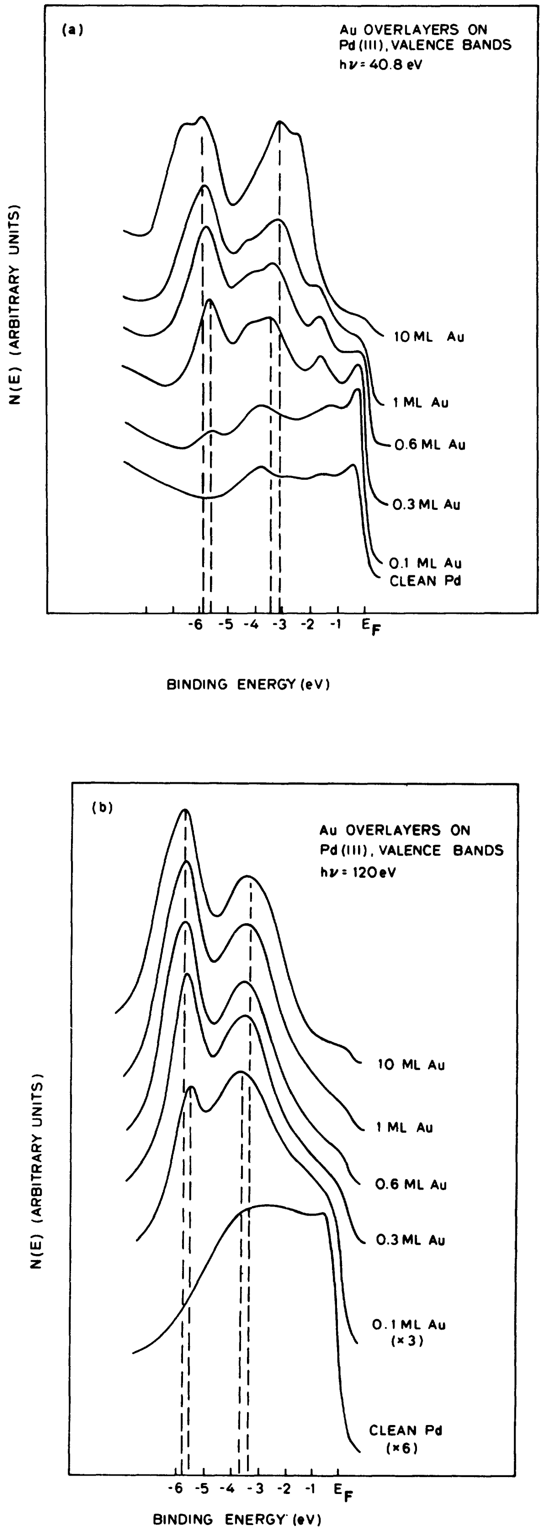

FIG. 1. Valence-band PES spectra of Au overlayers on Pd(111) as a function of overlayer thickness at (a) $h\nu=40.8$ eV and (b) $h\nu=120$ eV.

d bands, more degenerate with the Au *sp* band. In addition, a structure at -4.2 eV is visible for Au coverages between 0.3 ML and 1 ML. It is relatively the strongest for 0.3 ML and does not appear to merge into the Au structure at high coverages. We, therefore, tentatively identify it as a hybrid structure due to the Pd-Au interaction.

C. Au diffused into Pd

We will next compare the Au overlayers and Au diffused into the Pd matrix. The diffusions were achieved by very short (15—30 sec) heatings to $\sim 400\,^{\circ}\mathrm{C}$. The heatings were continued until a significant change in the valence-band structure at 120 eV could be observed and until the height of the Au $4f$ core level (as measured by photoemission at $h\nu = 120$ eV) was reduced by at least 20%. Figures 2(a) and 2(b) show three examples of comparison between Au evaporated onto the surface and Au diffused into the Pd for $h\nu = 40.8$ and 120 eV. In each case, for both photon energies, the same effect occurs. The higher-binding-energy gold structure moves toward E_F, while the gold structure closer to the Fermi level remains at essentially constant binding energy. Thus, the separation between the spin-orbit-split gold peaks decreases as the Au diffuses into the Pd, and at the same time the Au structure is centered at lower binding energy for the diffused gold. The decrease in the separation between the gold peaks can be easily explained; it appears to be a direct result of the more atomic nature of the gold when it is diffused into the Pd with a larger average Au-Au separation. This effect produces a spin-orbit splitting closer to the value for atomic Au, which was mentioned earlier to be 1.5 eV. For example, the $5d$ splitting for the 0.3-ML overlayer at 120 eV is ~ 2.0 eV, whereas it decreases to ~ 1.6 eV when the Au is diffused. The effect of the shift to lower binding energy of the center of the Au structure is a somewhat less obvious result of the diffusion; it will be addressed in the discussion section.

D. Stabilized alloy

The final portion of the study involved the formatoin of a stabilized alloy surface. This was accomplished in the following way. A very large (>20 ML) evaporation of Au was performed. Successive (5—10)-min anneals were carried out to $800\,^{\circ}\mathrm{C}$, until further 10-min anneals caused negligible change in the Au concentration (measured by comparing the Au 69-eV Auger-peak height to the Pd 330-eV Auger-peak height). This is a rather novel method of forming a stable alloy surface; it was patterned after the work of Helms and Yu[4] on the Pt-Cu sys-

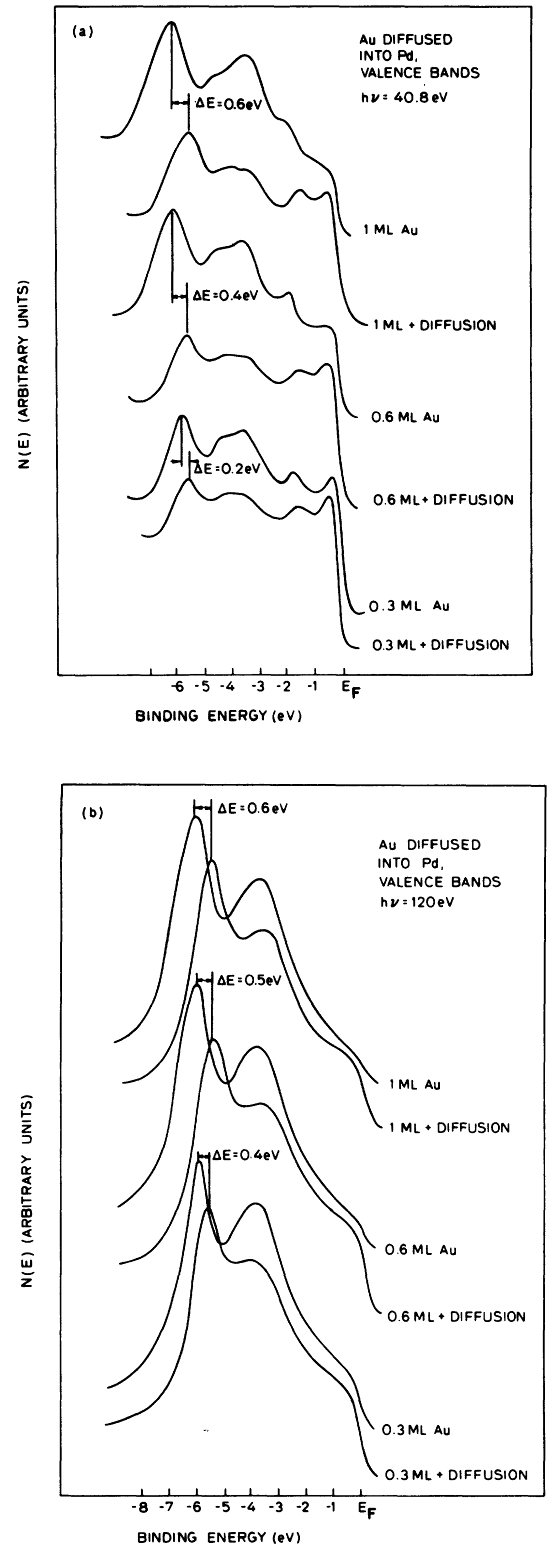

FIG. 2. Valence-band PES spectra of Au overlayers on Pd(111) before and after diffusion at (a) $h\nu = 40.8$ eV and (b) $h\nu = 120$ eV.

tem. This technique was necessitated by the unavailability of good commercially grown single crystals of Pd-Au, but it actually has inherent advantages over the use of Pd-Au single crystals. Depending on the temperature chosen for the anneal, the composition in the surface region will stabilize at different values due to the change in diffusion coefficient with temperature.[15] The ideal expression for the concentration of Au in the surface layer is

$$C_{\mathrm{Au}}(X=0,t)=\operatorname{erf}\left[\frac{d}{\sqrt{4Dt}}\right],$$

where d is the initial evaporated Au thickness, D is the (temperature-dependent) diffusion coefficient of Au in Pd, and t is time.[15] After some time t has elapsed at a certain value of D (corresponding to an anneal), changes in t of 1000 sec or so at that same temperature cause only small changes in the value of $C_{\mathrm{Au}}(X=0,t)$. This corresponds to the stabilized surface. Yet, the value of this stabilized $C_{\mathrm{Au}}(X=0,t)$ depends on D. Thus, by choosing different values for the annealing temperature, one can form a series of stabilized alloy surfaces of different compositions from one single-crystalline sample. In this study the annealing temperature was chosen to be ~800 °C because future experiments were planned for this crystal involving oxygen adsorption. Desorption of the oxygen involves ~10-sec heatings to 750 °C, and therefore the Pd-Au surface had to be stabilized at a temperature greater than 750 °C so that these short heatings to 750 °C would not change the surface composition. Within those constraints it was desired to have the largest possible Au concentration in the stable suface, so 800 °C was chosen as the annealing temperature. The sample was annealed for ~1800 sec to achieve a fairly stable concentration. The relative heights of the Au 69-eV and Pd 330-eV AES peaks as a function of annealing time and temperature are listed in Table I.

Experimental determinations of the stabilized surface Au concentration can be fairly accurate as will be shown below. Calculation of the stabilized concentration from published values of diffusion constants is rather unfeasible due to the huge variation of the diffusion constant with concentration and temperature.[15] The percentage of Au in the surface region of the stabilized alloy was estimated in the following way.

At $h\nu=120$ eV the emitted valence-band electrons have kinetic energies of ~100–115 eV. At these energies their escape depth is *quite* short[11] (<5 Å), and therefore the photoemission curves correspond mainly to the surface layer of atoms. We compare the valence-band structure of the stable alloy at $h\nu=120$ eV [shown in Fig. 3(a)] with those of the various submonolayer overlayers [shown in Fig. 1(b)]. In particular, the relative heights of the Pd-derived structure just below E_F and the Au-derived peak at ~ −5.7 eV are compared. It is found that the stabilized alloy corresponds most closely to the 0.3-ML overlayer. We can conclude that the surface layer of the stable alloy has a composition of ~30 at.% Au (±10%). It is not totally clear whether there is appreciable surface segregation in this case. AES can shed little light on the question, since the large Pd peak (at 330 eV) is far from the large Au peak (69 eV) and their escape depths are not the same. The escape depths are not known closely enough to do an accurate quantitative analysis. The quasichemical theory of surface segregation developed by Williams and Nason[16] predicts little or no surface segregation in the Pd-Au system since the heats of sublimation are quite similar for Pd (90 kcal/mole) and Au (88 kcal/mole).[17] Experimental data from the literature is conflicting: no surface segregation was detected for microspheres of Pd-Au,[18] while some surface Au enrichment was seen for polycrystalline foils.[17] To the author's knowledge no results have been reported for single crystals of Pd-Au. We will assume that the Au concentration in the near-surface region is not drastically different from that in the surface layer, and therefore that the surface region of the stabilized alloy corresponds fairly well to a single-crystalline Pd-Au alloy with ~30 at.% Au concentration. Figure 3(b) shows the valence bands of the stable alloy versus the 0.3-ML overlayer of Au at $h\nu=40.8$ eV. There is a reasonable correspondence in the relative magnitudes of the Pd- and Au-derived structure for the alloy and the overlayer which supports the idea that the stabilized alloy is ~30 at.% Au in the near-surface region sampled by the 40.8-eV light.

From Figs. 3(a) and 3(b) it is clear that the major features of the alloy and the 0.3-ML overlayer are

TABLE I. Stabilization of Pd-Au crystal by annealing.

Incremental anneal time (sec)	Temperature of anneal (°C)	Ratio of Au 69-eV/Pd 330-eV peak heights after anneal
No anneal		12.0
30	540	9.55
30	590	6.94
30	640	2.21
90	670	1.20
300	680	0.80
330	760	0.415
330	770	0.355
300	770	0.304
300	780	0.284

the same. More of the details are apparent at $h\nu=40.8$ eV. The structures at -3.4 and -5.6 eV (which were shown to merge smoothly into the Au structure for increasing overlayer coverage) still remain in the alloy at -3.4 and -5.2 eV. The structures at 0.4 and 1.6 eV, close to the positions of the clean Pd peaks, are still sharper and stronger in the alloy than for pure Pd. And, the additional structure at -4.2 eV, which for the overlayers did not correspond clearly to either Pd or Au structures, also remains in the alloy at ~ -4.0 eV. The main change betwen the overlayer and the alloy is a slight narrowing of the Au structure for the alloy and a slight shift of the center of the Au structure to lower binding energy.

Figure 4(a) shows the Pd-Au alloy structure as a function of photon energy. Clean Pd spectra for some of the same energies are also shown in Fig. 4(b). Two main effects are seen. First of all, the alloy does seem to be richer in structure than the pure Pd in the region within 2 eV of the Fermi level, although the Au *d* bands do not extend upward that far. The second effect is that for the alloy the structures near E_F move with photon energy, giving evidence for direct transitions remaining in the alloy. The changes in the relative strengths of the Pd and Au structures with photon energy are due to the Cooper minimum in the Pd $4d$ photoionization cross section evidenced at $h\nu=120$ eV.

IV. DISCUSSION

The case of Au on Pd is a good example of a nearly ideal alloy: it forms a random substitutional alloy at all component ratios. Of particular note for this study is the considerable valence overlap. We have followed the electronic structure throughout the entire process of formation of a Pd-Au alloy. We are thus able to look at the following situations involving the Pd-Au system:

(1) Thin overlayers of Au on Pd can be compared with bulk-type Au.

(2) We can compare the submonolayers of Au on the Pd surface (a two-dimensional situation) with the Au dispersed in the three-dimensional Pd lattice.

(3) We can compare the structure of the Pd-Au alloy with those of the pure bulk components.

A. Au Overlayers on Pd

1. Comparison between Pd-Au and Cu-Zn

We will start by examining thin layers of Au on Pd, as compared to thin layers of Cu on Zn (Abbati *et al.*).[1] We have found for Pd-Au that new structure appears for Au coverages as low as 0.1 ML, which evolves gradually and smoothly into structure

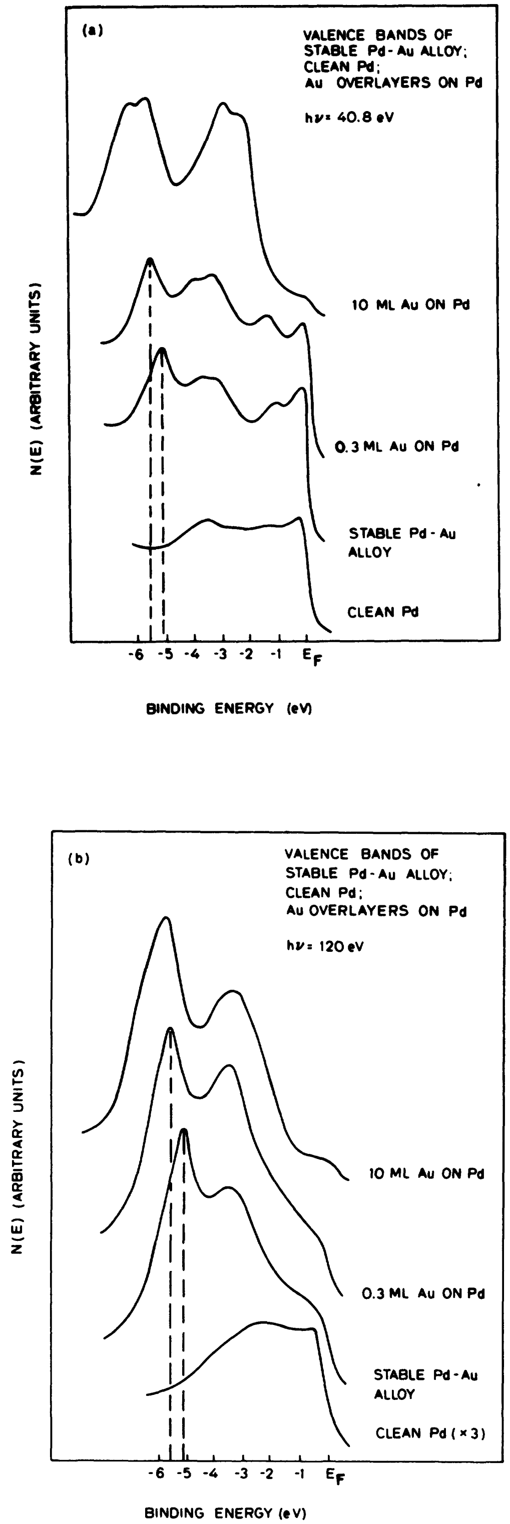

FIG. 3. Valence-band PES spectra of Au overlayers on Pd(111) and stabilized Pd-Au alloy at (a) $h\nu=40.8$ eV and (b) $h\nu=120$ eV.

characteristic of bulk Au [this is most easily seen from the data at $h\nu = 120$ eV in Fig. 1(b)]. The Au *d* bands are narrower for overlayers up to 1 ML thick than for bulk Au due to smaller Au-Au interactions which give rise to more atomiclike structure. The center of the Au structure remains at ~4.6-eV binding energy during the entire series, from 0.1 ML Au through 10 ML. The major effects, then, of going from bulk Au to a thin layer of Au on Pd are (1) a decrease in the splitting between the Au spin-orbit-split peaks, (2) the appearance of additional structure at 4.2 eV caused by the Pd-Au interaction, and (3) the sharpening of the structures near E_F which are above the Au *d* bands. The position of the Au 5*d* structure remains essentially unchanged.

In contrast, Abbati *et al.*[1] performed photoemission on an ordered ML of Cu on Zn(0001) as an example of a nondegenerate system (i.e., the Zn *d*-band peak is at ~9.9-eV binding energy, whereas the Cu *d*-band peak falls at ~3.0-eV binding energy). As in the present case, the Cu *d*-band structure narrows (by at least 1 eV) in going from bulk Cu to the Cu overlayer. However, the center of gravity of the Cu valence structure shifts by about 1 eV to a higher binding energy for the thin layer. In contrast to our results, no evidence of Cu-Zn hybridization was seen. They were able to achieve fairly close theoretical agreement with the use of tight-binding calculations of a slab of 13 atomic planes of Zn plus one plane of Cu on either side of the slab. They also found their experimental results to be in basic agreement with calculations for an isolated ML of Cu. The reason given for the shift to higher binding energy was charge "decompression" of the Cu *sp* electrons at the surface relative to the bulk. This would tend to decrease the electron screening at the surface. In the case of Au on Pd no such shift occurs. The fact that the structures near E_F above the Au *d* bands change with the addition of the Au overlayer points to a hybridization of the Au *sp* electrons with the Pd *d* electrons. As a result, the Au *sp*'s may become more localized than purely *sp* electrons in bulk Au. Thus, the decompression effect at the surface may be suppressed, and with it, the shift to higher binding energy.

Eastman and Grobman[2] did photoemission studies of thin overlayers of Cu and Pd on Ag. These systems are more similar to ours in that there is some overlap between the *d* bands of the metals (though there is greater overlap for Pd and Au). They report that the overlayer *d*-state resonance lies closer to the Fermi level than the center of the corresponding resonance for the bulk metal in both cases. Their results, then, more closely correspond to those of the present study. However, Eastman

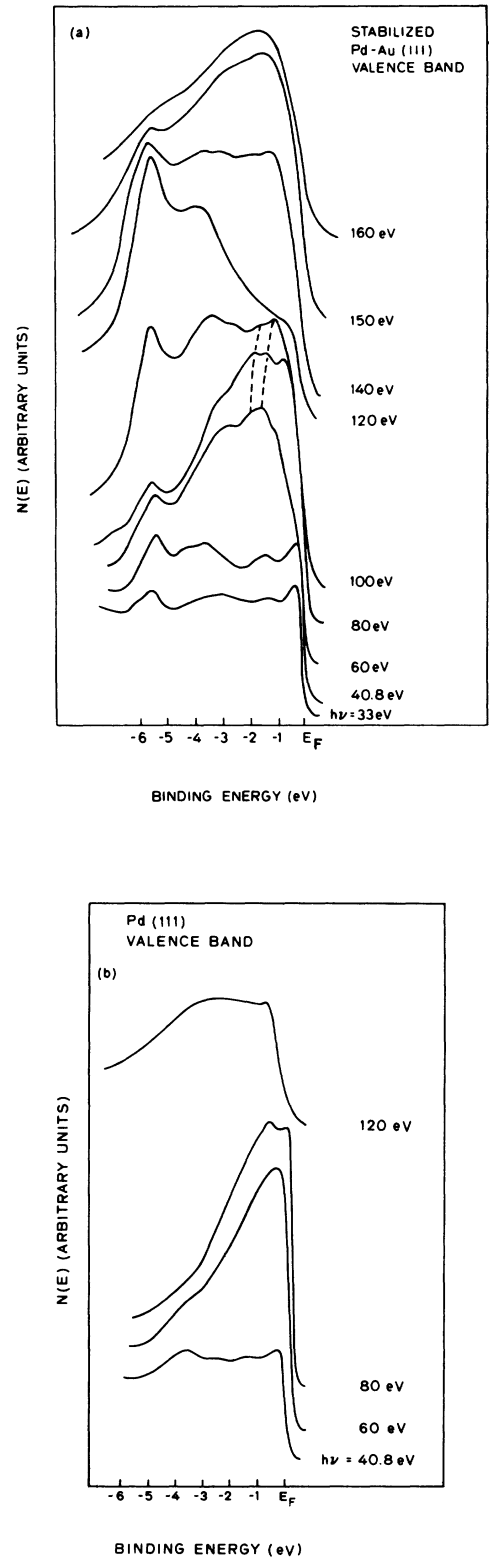

FIG. 4. Valence-band PES spectra of (a) stabilized Pd-Au alloy and (b) clean Pd(111) as a function of $h\nu$.

and Grobman were limited to photon energies less than 11.6 eV, and were therefore unable to clearly see the entire valence-band structure of the overlayers.

2. *Structures near E_F*

The sharpening and enhancement of the structures near E_F (at the positions of the clean Pd peaks) upon addition of up to a ML of Au is a striking and unusual phenomenon. Though the effect remains to some extent for 1 ML Au overlayer and for the stabilized alloy, it is the strongest for the 0.3-ML overlayer. It almost appears as though the Pd-Pd lattice separation had increased, producing a sharper, more atomic Pd spectrum. This model cannot explain the effect, however, for the following reasons. (1) The Pd structures near E_F are direct transition peaks [whose positions move with changing photon energy, as seen in Fig. 4(b)]. Thus, these structures would tend to be suppressed rather than strengthened by a weakening of lattice periodicity. (2) The Pd and Au lattice parameters are similar [3.89 Å for Pd, 4.08 Å for Au (Ref. 19)]. But, if this 5% difference were to be the cause of a change in the Pd valence structure, the changes would be the most pronounced for the stabilized alloy where a larger percentage of the Pd atoms seen in the PES data would have Au neighbors than for the Au overlayers. Thus a change in the lattice parameter is not a sufficient explanation for the sharpened structures near E_F.

It would also be tempting to attribute the effect to hybridization between the Pd $4d$ valence electrons and the overlapping Au *sp* electrons. Once again, however, this is an unsatisfactory explanation, since an *spd* hybrid would tend to be less localized than a purely *d*-like electron and would therefore result in broader rather than sharper structure. It might be worthwhile to investigate the possibility that the Au *sp* electrons may be screening the Pd electrons and thus reducing the *d* interactions between neighboring Pd atoms.

There are no obvious phenomenological explanations for the enhancement of the structures near E_F upon evaporation of thin overlayers of Au on Pd. But it is clear that the effect remains even for the stabilized alloy. As will be seen later, during the discussion of the alloy data, there has been some experimental evidence for a similar (though less pronounced) effect in the Cu-Ni system.

B. Au diffused into Pd

We next consider the changes which occur as the Au is diffused into the Pd matrix. These consist of (1) a narrowing of the Au-derived structure, and (2) a slight shift of the Au-derived structure to lower binding energy. We have already discussed the narrowing and attributed it to the larger average Au-Au distance which produces a more atomiclike spin-orbit splitting. A similar effect is seen for the Au-In system when an evaporated Au layer is alloyed with In.[6] It also appears for the Au-Al (Ref. 20) and Au-Cd (Ref. 21) systems.

The shift of the Au-derived structure to lower binding energy is a somewhat more complex phenomenon. It could possibly be a simple consequence of the fact that the Au atoms in the three-dimensional Pd lattice have a larger number of nearest neighbors than those in an overlayer. An increase in the number of neighboring Pd electrons available to provide screening for the emitted Au electrons could cause the shift to lower binding energy. The Pd atoms could have a substantial screening effect due to the large density of electrons at the Fermi energy. And yet, when Au forms a three-dimensional alloy with In, the Au bands shift to *higher* binding energy.[6] The answer to this apparent inconsistency may lie in the *d*-band overlap in the Pd-Au system which results in some Pd-Au hybridization. In contrast, the In *d* bands are ~17 eV below E_F and there is no overlap with the *d* bands. Thus the Au in In is in a situation closer to that of isolated atoms suspended in a free-electron gas. In contrast, the Pd-Au hybridization places the Au atoms in a more metalliclike, less atomiclike situation. This is further borne out by the direct transitions which seem to be still present near E_F for the Pd-Au alloy. (This will be discussed in more detail below.)

C. Stabilized Pd-Au alloy

As was mentioned earlier, the main features of the stabilized ~30 at. % Au-alloy surface region are very similar to those of the 0.3 ML Au overlayer for PES at 40.8 and 120 eV. The main changes between the overlayer and the alloy is a slight narrowing and further shift to lower binding energy of the Au-derived structure. This could be attributed to a slight increase in the average Au-Au distance upon alloying—perhaps due to a small amount of clustering of the Au atoms in the overlayer. Or it may be a more complicated result of the alloying process, related to the increase in the average number of Pd nearest neighbors for the Au atom upon moving into the Pd matrix.

The Pd-Au alloy curves in Fig. 4(a) show more structure within 3 eV of E_F than the corresponding Pd curves in Fig. 4(b), particularly at 80- and 100-eV photon energy. As was seen earlier, there is no simple phenomenological explanation for this effect, either for the thin overlayer case or for the alloy case. However, a similar, though less pronounced, effect is also seen via PES in the Cu-Ni system,[23] whereby alloying Ni with Cu causes substructure to appear above the Cu *d* bands in the presumably Ni-derived spectrum, which is somewhat more visible than that seen in the photoemission of pure Ni. One difference is that, in the Cu-Ni system, the stronger substructures are seen mainly for the photon energies which show predominantly bulk structures (~7–10 eV). Whereas, for the Pd-Au system, the substructure is seen for such surface-sensitive photon energies as 80 and 100 eV.

The last striking effect for the stable alloy is the persistence of sharp direct transition structure near E_F, even though Pd-Au is a random substitutional alloy with no long-range order. Once again, a similarity has been seen in the Cu-Ni system (Yu *et al.*[23]) and more recently in the Pd-Ag system (Pessa *et al.*[5]) for photon energies as high as 40.8 eV. As in the Pd-Au case, the structures within 3 eV of E_F seem to have the greatest photon-energy dependence for Cu-Ni and Pd-Ag, and also, in the Pd-Ag case, the greatest angular dependence.[5]

There has been much consideration given to the concept of band structure in random substitutional alloys. Bansil *et al.*[23] suggested that an alloy band structure can exist due to the remaining effects of lattice periodicity. They formulated a complex alloy band structure for the Cu-Zn system with the use of the averaged *T*-matrix approximation (ATA).[24] The effect of alloying in this case is to broaden the energy bands and to weaken but not eliminate direct transitions. Recent calculations have been made by Temmerman *et al.*,[25] (Gordon *et al.*,[26] and Pindor *et al.*[27] on the Cu-Ni and Pd-Ag systems with the use of the Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA) method.[28] In their method, a configurationally averaged "Bloch spectral function" $A_B(k,\epsilon)$ is calculated, whose integral over the Brillouin zone is the averaged density of states. $A_B(\vec{k},\epsilon)$ corresponds to the density of states at wave vector $\vec{k}$ in the first Brillouin zone. For a system with long-range order, $A_B(\vec{k},\epsilon)$ becomes a set of δ functions, whereas for the disordered case the peaks broaden out. The width of the peak $\Delta E_{k,\nu}$ (where ν is the band index) corresponds to the inverse lifetime of a state of wavevector $\vec{k}$. If the spectral function peaks are well separated compared to their widths, the alloy is considered to have a well-defined band structure. Once again, in this formulation, the effect of alloying is a broadening and smearing of the direct-transition structure of the pure materials.

In contrast to these theoretical treatments of the band structure itself, our experimental energy-distribution curves (EDC's) in Fig. 3(a) show an actual sharpening of the direct-transition structures near E_F in the Pd-Au alloy system. Two interpretations are possible. One could assume a correlation between the width of the structure in the EDC's and the widths of the initial ground-state band structure. This would lead to the conclusion that the existing ATA and CPA calculation methods are not as yet sophisticated enough to completely explain the results on Pd-Au, and that more detailed theoretical calculations are necessary.[29]

A second interpretation of our experimental results could be that the changes in the EDC's upon alloying are due completely to excitation effects, e.g., a change in screening or other many-body effects. This would be evidence that final-state effects mask the band-structure effects in the pure Pd EDC's, but that these final-state effects are removed by alloying with Au.

V. SUMMARY AND CONCLUSIONS

The Pd-Au system has been studied over conditions ranging from submonolayer Au overlayers on Pd to a stabilized Pd-Au alloy region. We find that the valence-band electronic structure is similar for the 0.3-ML overlayer and the ~30 at. % Au alloy. The salient features of the PES spectra are the following:

(1) Structures near the energies of the pure Au 5*d* peaks (which merge smoothly into the Au structure with increasing Au thickness).

(2) Structures near the energies of the pure Pd 4*d* peaks, which are sharper and stronger than for pure Pd.

(3) Movement of these structures near E_F with changing photon energy, indicating direct transitions remaining in the random substitutional alloy.

(4) A new structure not clearly identified with either Pd or Au, which presumably results from Pd-Au hybridization upon alloying.

Many of these features are similar to the Cu-Ni system and have been seen in multiple-scattering calculations on Cu-Ni. Yet, further theoretical developments are necessary to explain other features such as the increased sharpness of the direct-transition structures near E_F upon alloying. To the author's knowledge, no calculations have been done on Pd-Au alloys. We believe that such calculations could be quite useful. First of all, they would increase the sophistication of theoretical methods. Second, the Pd-Au system is potentially important in areas such as catalysis,[30] and therefore insights into its electronic structure could be extremely valuable.

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