

## Quantum-Well States in a Metallic System: Ag on Au(111)

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Quantum-well states have been observed with angle-resolved photoemission for Ag overlayers with thicknesses up to 40 monolayers epitaxially grown on Au(111). These states are observed within an energy window of 1 eV. The complementary system, Au on Ag(111), exhibits no such states. The results can be explained in terms of the band-structure mismatch between Au and Ag. The coherence length of the states and quasibound quantum-well resonances will be discussed.

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Quantum-well states are well known in systems containing semiconductors and insulators, such as the GaAs-Al<sub>x</sub>Ga<sub>1-x</sub>As family.<sup>1,2</sup> These states are quantized electronic states confined within a thin slab, and can be roughly described in terms of the usual one-dimensional quantum-box problem given in any standard quantum mechanics textbook. For instance, semiconductor quantum wells support these states near the edges of the fundamental gap where the band-gap mismatch leads to electron confinement. Such states play an important role in the operation of many optoelectronic devices (e.g., the "quantum-well" laser). Quantum-well states in purely metallic systems, on the other hand, have not been observed before, as far as we know. For lack of an absolute gap, an electron in a metal can usually propagate through a metal-metal interface; such a "leaky" interface cannot lead to electron confinement.

At an interface, the question of electron reflection versus transmission depends on the mismatch of material properties. If two materials are very similar, the interface between them will be less likely to reflect electrons. Au and Ag have nearly perfectly matched lattices. Their band structures are also very similar. Thus, the Au-Ag system would seem to be one of the worst possible candidates for observation of quantum-well states. Yet we have observed such states in Ag films epitaxially grown on Au(111) with angle-resolved photoemission. These states exist in an energy window of about 1 eV. A similar set of experiments performed on the complementary system, Au on Ag(111), revealed no such states. These findings can be explained in terms of the band-structure mismatch between Ag and Au (even though the mismatch is small). The key issue here is that the electron dynamics (transmission and reflection) at an interface is determined by both energy and crystal-momentum conservation. Thus, even without an absolute gap, electron confinement is still possible near the edge of a "relative" gap. The quantum-well states are observed for Ag films as thick as 40 monolayers (ML); this limit is due to our experimental energy resolution. The coherence length of the states is therefore rather

long. Photoemission is known to be mainly a surface-sensitive technique; this experiment demonstrates the interesting possibility of probing the effects of a deep interface.

The photoemission experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin-Madison at Stoughton, Wisconsin. A Seya monochromator and a 6-m toroidal-grating monochromator were used for dispersing the synchrotron radiation during separate runs. The photoemitted electrons were analyzed with a hemispherical analyzer having a full acceptance angle of 3°. The Ag(111) substrate was prepared by cycles of Ar-ion sputtering and annealing. The Au(111) substrate was prepared by epitaxial growth of a thick film of Au on Ag(111). Au and Ag deposition was done with feedback-controlled electron-beam bombardment of tungsten crucibles containing ultrapure Ag and Au. The rate of evaporation was determined with a quartz thickness monitor; the absolute film thickness was uncertain by about  $\pm 10\%$ .<sup>3</sup> The deposition was done at a sample temperature of 30–50°C to avoid Ag-Au intermixing. The sample quality was checked with electron diffraction and Auger spectroscopy. Previous studies had shown that Au-Ag systems prepared in this manner exhibited nearly ideal interface configurations and excellent overlayer smoothness.<sup>4-6</sup>

Figure 1 shows angle-resolved photoemission spectra taken from Au(111), Ag(111), Ag(111) covered by 20 ML of Au, and Au(111) covered by 20 ML of Ag. The emission direction of the photoelectrons is normal to the sample surface, and the photon energy is  $h\nu=10$  eV. The Au(111) and Ag(111) surfaces have been examined in the past with photoemission by many authors<sup>6-9</sup>; our results are in substantial agreement with theirs. To explain the origin of the various peaks, we show in Fig. 2 the relevant portions of the band structure of Ag and Au for  $\mathbf{k}$  along the sample surface normal which is the direction probed by the photoemission experiment. Below the Fermi level  $E_F$ , each material has a nearly-free-electron-like "sp" band with its maximum ( $L_4^-$  critical point) at the  $L$  point in the Brillouin zone (the origin of

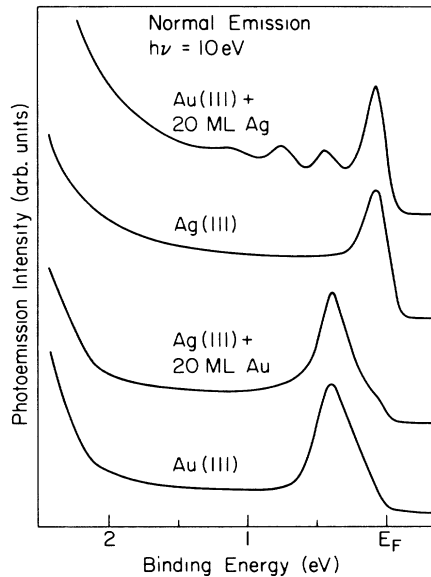


FIG. 1. Normal-emission spectra taken with a photon energy  $h\nu=10$  eV for, from bottom to top, Au(111), Ag(111) covered by 20 ML of Au, Ag(111), and Au(111) covered by 20 ML of Ag. The binding-energy scale is referred to the Fermi level  $E_F$ .

the horizontal axis). Above this  $sp$  band is a relative gap (the " $L$  gap"); within this gap, there is a surface state just below the Fermi level (indicated by a horizontal line). The  $L$  gap is a relative gap, because there exist bands within this energy range for  $k$  along other directions in the Brillouin zone.<sup>10,11</sup> The  $sp$  band disperses downward for increasing  $k$  toward the  $\Gamma$  point, and crosses many " $d$ " bands. Only the uppermost  $d$  band of Au is shown in the diagram. The uppermost Ag  $d$  band is at a binding energy of about 4 eV, outside the energy range shown. The band structures shown in Fig. 2 are accurate only to about  $\Delta E=0.1$  eV and  $\Delta k=0.03 \text{ \AA}^{-1}$ , because of uncertainties and variations in the reported experimental and theoretical results.<sup>6-11</sup>

The Au(111) spectrum in Fig. 1 shows one peak located just below the Fermi level, which is derived from the surface state in the  $L$  gap. The rising slope on the high-binding-energy end of the spectrum is the tail of a peak derived from the direct transition from the topmost Au valence  $d$  band (see Fig. 2). There are no other features between the  $d$  band and the surface state in the spectrum, as the direct transition peak derived from the  $sp$  band is at an energy outside the range shown.<sup>7</sup> The Ag(111) spectrum in Fig. 1 also shows a surface-state peak just below the Fermi level. The tail on the high-binding-energy end is part of the direct-transition peak from the  $sp$  band.<sup>9</sup> In Fig. 1, the spectrum for 20 ML of Au on Ag(111) looks essentially the same as that for Au(111), perhaps to no one's surprise, as it is often assumed (and shown) that an overlayer more than a few

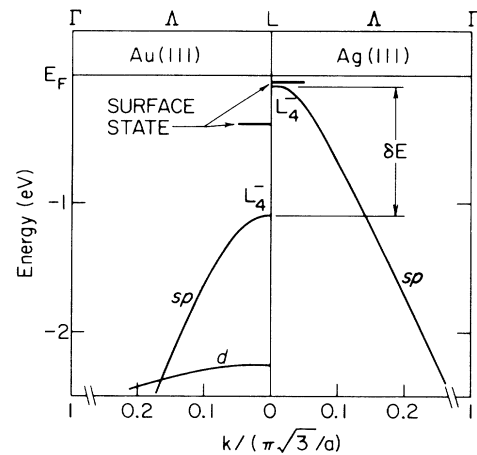


FIG. 2. Valence-band dispersion curves for Ag(111) and Au(111) along the [111] direction. For each system, a surface state is indicated. The wave vector  $k$  is measured in terms of  $\pi\sqrt{3}/a$ , where  $a=4.09 \text{ \AA}$  is the lattice constant for both Ag and Au. The energy window  $\delta E$  for the quantum-well states is indicated.

monolayers thick should show essentially bulklike photoemission spectra.<sup>12</sup> The surface state looks somewhat sharper, because the spectrum was taken with a higher resolution. The evolution of the surface state as a function of overlayer thickness has been discussed in a previous publication.<sup>6</sup> The spectrum for 20 ML of Ag on Au(111) in Fig. 1, however, appears qualitatively different; when compared with the Ag(111) spectrum, two extra peaks can be clearly seen at binding energies of 0.5 and 0.8 eV. We will show evidence below that these are quantum-well states derived from the Ag  $sp$  states. A third, much weaker peak can also be seen at a binding energy of about 1.1 eV, which is another quantum-well state just emerging (see below).

To describe the quantum-well states, consider a simple physical picture in which an electron bounces back and forth within the Ag film. The electron motion within the film is well described by the same Hamiltonian as that for bulk Ag; thus the motion is characterized by the dispersion curve  $E(k)$  shown in Fig. 2. A stationary state is formed with the round-trip phase shift of the wave function satisfies the usual quantization rule:

$$2kd + \delta_1 + \delta_2 = 2n\pi, \quad (1)$$

where  $n$  is any positive integer,  $k$  is the wave vector,  $d$  is the Ag film thickness, and  $\delta_{1,2}$  are the phase shifts at the two boundaries upon reflection. For a given quantum number  $n$ , a change in  $d$  would yield a corresponding change in  $k$ , since  $\delta_{1,2}$ , being interface properties, are relatively insensitive to the change in  $d$ . The energy of the state should change correspondingly according to the dispersion curve  $E(k)$  shown in Fig. 2. Indeed, Fig. 3

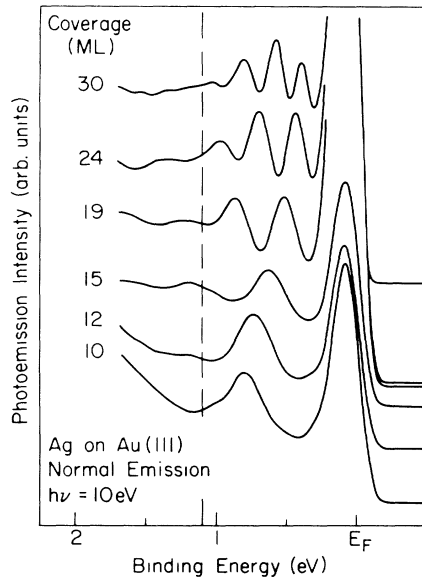


FIG. 3. Normal-emission spectra taken with  $h\nu = 10$  eV for Ag overlayers with indicated thicknesses on Au(111). The vertical dashed line indicates the onset for emergence of the quantum-well-state peaks.

shows that these quantum-well states evolve as a function of  $d$  in the manner expected; the states move closer to the Fermi level (hence smaller  $k$  values in Fig. 2) for increasing Ag film thicknesses. In the process of the evolution, more peaks become visible. We have observed resolved peaks up to a thickness of 40 ML; beyond that point the states become too crowded to be resolved with our equipment. To verify that the peak separations in Fig. 3 are indeed described by Eq. (1), we note that  $\Delta k$ , the difference in  $k$  values between two neighboring peaks (with  $\Delta n = 1$ ), should equal  $\pi/d$  plus a correction term corresponding to the energy dependence of the phase shifts. The latter quantity is unknown, but is expected to be much smaller than  $\pi/d$ . Using the band dispersion shown in Fig. 2 to determine the  $k$  values, we obtain for the data shown in Fig. 3 that  $\Delta k$  ranges from  $0.65(\pi/d)$  to  $0.8(\pi/d)$ . The departure from  $\pi/d$  has three possible contributions: (1) the phase-shifted correction term, (2) the uncertainty in the band dispersion as mentioned above, and (3) a 10% uncertainty in our absolute film-thickness determination.

The most interesting behavior here, however, is the apparent onset for emergence of the peaks as the overlayer thickness is increased. The onset is at about 1.1-eV binding energy, indicated by the vertical dashed line in Fig. 3; the quantum-well states are clearly observed only to the right of this dashed line. The onset coincides with the  $L_4^-$  critical point of Au (see Fig. 2); thus, the quantum-well states for Ag on Au exist only within the energy window  $\delta E$  between the Ag and Au  $L_4^-$  critical points. The reason for this behavior will now be ex-

plained. In addition to energy conservation, electron transmissions through an interface must satisfy the following condition for crystal-momentum conservation:

$$\mathbf{k}_{\text{Ag}} = \mathbf{k}_{\text{Au}} + \mathbf{k}_{\text{int}},$$

where  $\mathbf{k}_{\text{Ag}}$  and  $\mathbf{k}_{\text{Au}}$  are crystal momenta in Ag and Au, respectively, and  $\mathbf{k}_{\text{int}}$  is the crystal momentum provided by the interface. The Au-Ag interface is lattice matched; therefore, the interface potential step can provide crystal momentum only in the surface-normal direction. As a result,  $\mathbf{k}_{\parallel}$ , the component of  $\mathbf{k}$  parallel to the surface, is conserved. The problem reduces to a one-dimensional problem with  $\mathbf{k}_{\parallel} = 0$  for the photoemission geometry used, and bands in other directions not shown in Fig. 2, even though degenerate in energy, can be ignored. For Ag  $sp$  electrons within the energy window  $\delta E$ , energy conservation disallows the coupling into the Au substrate; therefore, quantum-well states are formed when the phase-shift condition is satisfied. For Ag states outside the  $\delta E$  window, the conservation laws can always be satisfied with Au states having the same energies, since the spectrum for  $\mathbf{k}_{\text{int}}$  is continuous; therefore, no quantum-well states are expected. This analysis also shows why no quantum-well states are observed in the complementary system, Au on Ag (see Fig. 1), since all of the states in the overlayer can be coupled to states in the substrate.

Several other experiments have been performed to further test the model presented above. Limited by space, only the essential points will be summarized here. The quantum-well states (and the absence of them) have been verified with many different photon energies. Indeed, if the states are truly confined within the overlayer, they should show no " $k_{\perp}$  dependence." Also, if the spectra for Ag on Au are greatly magnified in the vertical scale, one could notice the presence of extremely broad and weak "quantum-well resonances" outside the energy window  $\delta E$ . Note that the electron transmission through the interface for energies outside  $\delta E$  is generally not 100%. The partial reflection at the interface can yield quantum-well resonances if the phase-shift quantization rule is satisfied. The resonances are not truly confined within the overlayer. Apparently, they are highly damped in this system, accounting for the observed extremely low intensity and broad width. We have also observed quantum-well resonances for Ag overlayer films on a number of different substrates (Ni, Cu, Si, and Ge).<sup>13,14</sup> For highly mismatched substrates, the electron reflection at the interface becomes significant, and the resonances become more pronounced. This is opposite to the intuition that systems with better structural order should yield sharper spectral features. In theory, a careful analysis of the resonance line shape and intensity can allow a determination of the electron dynamics at the interface.

The structural perfection of the overlayer is evident

from an inspection of Fig. 3, for any significant thickness variation more than a few monolayers would smear out the spectral features. The results also imply that the coherence length of the wave function is rather long. The coherence length is at least on the order of the film thickness for the quantum-well states to exist. The largest thickness for which we have observed the quantum-well states is 40 ML; therefore, the coherence length is at least 100 Å. The group velocity of the Ag *sp* states is less than 8 eV Å in the region of interest (see Fig. 2); thus the energy broadening of the states is at most 0.08 eV. The peak widths observed in Fig. 3, greater than 0.08 eV, are most likely dominated by a small thickness variation of the film.

In summary, a "textbook case" of quantum-well states in metallic systems is presented. The results can be understood in terms of the band structure and electron dynamics at the interface. Limits on overlayer structural perfection and the coherence length of the states can be established. The experiment demonstrates that photoemission can be used to probe the effects of a deep interface. The band structure can also be deduced.<sup>15</sup>

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