Avoided Crossings of Au(111)/Ag/Au/Ag Double-Quantum-Well States

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A $Ag_8/Au_3/Ag_x$ double quantum well is grown on Au(111) to form two Ag quantum wells coupled through a thin Au barrier layer, and the electronic structure of this system is examined with angle-resolved photoemission. As the thickness of the outer well (x, in monolayers) is varied, the measured binding energies of the quantum-well states show an avoided-crossing behavior, in good agreement with a model calculation based on Bloch wave functions. The results demonstrate the effect of electronic translayer coupling.

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Electronic coupling through a thin film plays an important role in a number of areas of materials physics. A well known example is the periodic magnetic coupling of layered magnetic structures mediated by nonmagnetic spacer layers [1]. Although such magnetic systems are of great interest, they are rather difficult to model theoretically due to the complexity of the band structure of the materials involved. As a result, the detailed mechanism for the magnetic alignment is still a matter of debate. In this study, we examine a similar, although nonmagnetic system, for which a simple model based on Bloch wave functions describes the essential physics. This allows us to study a basic manifestation of electronic coupling through a thin film. The system that we choose to study is two Ag(111) quantum wells separated by a thin Au(111) barrier layer, created by sequentially depositing Ag, Au, and Ag films on a Au(111) substrate using molecular beam epitaxy. The electronic structure is then examined with angle-resolved photoemission. In the limit of an infinitely thick Au barrier, the quantum-well states in the two Ag wells are decoupled. As the thickness of the outer well is varied, the binding energies of the outer well states will change and sweep across the energies of the inner well states. Such level crossings must be avoided if there is any coupling between the two wells. By choosing a thin Au barrier thickness in our experiment to facilitate the coupling, we have indeed observed this effect. Spectroscopic studies of avoided crossings are not only interesting fundamentally, but are also useful for determining the coupling strength, because the magnitude of the coupling matrix element is simply one half of the gap of the avoided crossing. This coupling matrix element is essential for the modeling of more complex layer structures.

Photoemission spectra were obtained at the Synchrotron Radiation Center of the University of Wisconsin at Madison in Stoughton, Wisconsin. The procedures for substrate preparation and overlayer growth have been described previously [2]. The Ag/Au/Ag double quantum wells were grown on single-crystal Au(111), which was prepared by depositing a thick Au buffer layer on a Ag(111) substrate. The initial Ag(111) substrate, the Au(111) buffer layer, and the final multilayer configuration all exhibited sharp electron diffraction patterns and an intense Shockley surface state just below the Fermi level, indicating excellent surface quality. The thicknesses of the inner Ag well and the Au barrier were 8 and 3 monolayers (ML), respectively (note that Ag and Au are lattice matched to within 0.2%). The outer Ag well thickness was varied from $x=6$ to 30 ML in this study. In addition, Ag single quantum wells on Au(111), with and without a Au overcoat, were prepared and studied as a reference.

In the following, we will present first our theoretical predictions, based on information obtained from studies of single quantum wells [2,3], and then the new experimental results. Figure 1 summarizes the behavior of single quantum wells. The dashed curves labeled Q_n, for $n=1$–4, indicate the measured binding energies of Ag single-quantum-well states for various thicknesses x. They represent the outer well states of a double quantum well in the limit of an infinitely thick Au barrier. Note that quantum well states only occur for binding energies E below the Ag valence band maximum (VBM) at 0.33 eV, but above the Au VBM at 1.1 eV. Within this energy range, electrons can be confined to the Ag well, as they cannot propagate into the Au substrate. For $E > 1.1$ eV, electrons can propagate in both Ag and Au, allowing a continuum of resonances, while for $E < 0.33$ eV electrons cannot propagate in either Ag or Au, so only surface (interface) states are allowed. The horizontal line labeled S in Fig. 1 indicates a Shockley surface state for this system [2]. In the limit of an infinitely thick Au barrier, the inner well becomes an 8 ML Ag well bounded on both sides by semi-infinite Au. Only one inner well state (labeled I) is allowed, and since it is decoupled from the outer well, its binding energy will be independent of x (as is indicated by the horizontal dashed line at $E=0.67$ eV in Fig. 1). Because state I is deeply buried, it is inaccessible using photoemission (due to the finite escape depth of the photoelectrons), and its binding energy must be extrapolated from less deeply buried wells. Note that state

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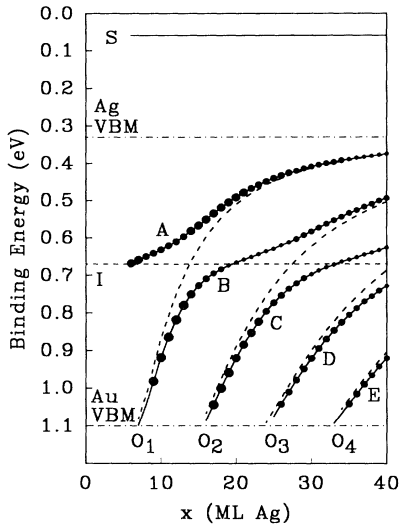

FIG. 1. Theoretical binding energies (circles) for the double-quantum-well system Au(111)/Ag_8/Au_3/Ag_x as a function of outer well thickness x. The area of each circle is proportional to the photoemission intensity. These circles are connected with solid curves (A-E) for clarity. The dashed curves show binding energies for isolated inner (I) and outer (O_n, $n=1$-4) well states. The energy positions of the Au and Ag VBM and the Shockley surface state (S) are also indicated. The binding energy scale is referred to the Fermi level.

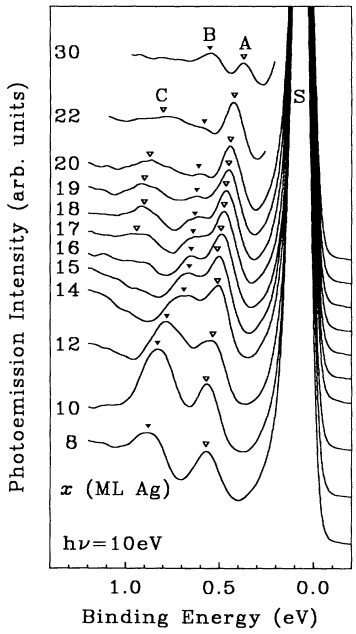

FIG. 2. Normal-emission angle-resolved photoemission spectra for various outer well thicknesses (x, in ML Ag). All spectra have been normalized to the incident photon flux. A surface state (S) and three double-quantum-well states (A,B,C) are labeled. The binding energy scale is referred to the Fermi level.

I intersects O_1 and O_2 at $x=14$ and 28 ML, respectively, so the states involved are degenerate for decoupled quantum wells. In these places we expect to observe avoided crossings if the Au barrier thickness is made finite (3 ML in our experiment).

In our model calculation, we employ a two-band approximation for the sp band of Ag and Au, which yields the lowest-order wave functions within the pseudopotential formalism [2,4]. These bulk wave functions are used for the entire width of each layer. This is expected to be a fairly good approximation, because the screening lengths in Ag and Au are very short ($\sim$0.5 Å), so the electrons will be in approximately bulklike environment for most of the layer thickness. These wave functions are either propagating (for energies within a valence band) or nonpropagating (for energies in a gap). For the vacuum barrier, a linear potential approximating the surface dipole layer is used. The slope of the potential is the only free parameter, and it is adjusted to reproduce the observed Shockley surface state near [4]. Since the wave functions are now fully defined throughout the entire system, all that remains is to match all of the boundary conditions; the allowed states will occur at binding energies for which all boundary conditions can be satisfied.

The calculated energies of these allowed states are presented in Fig. 1 with circles. The avoided crossings are apparent. For example, state A starts out as state I for small x, becomes a mixture of I and O_1 at $x=14$, and finally becomes O_1 for large x. Likewise, state B evolves from O_1, to a mixture of I and O_1 at $x=14$, to mostly I at $x=20$, to a mixture of I and O_2 at $x=28$, and finally to O_2. The two gaps of the avoided crossings at $x=14$ and 28 ML are 0.17 and 0.12 eV, respectively, which create substantial differences in binding energy between the coupled and decoupled states.

The angle-resolved normal-emission photoelectron spectra from Au(111)/Ag_8/Au_3/Ag_x for increasing values of x are shown in Fig. 2. The Shockley surface state (S) and three states derived from the quantum wells (A, B, and C) are labeled. The binding energies and intensities of these peaks as functions of x are summarized in Fig. 3, where the size of each circle is proportional to the emission intensity. Also shown in the figure (with dashed curves) are the corresponding theoretical results from Fig. 1. The agreement is quite good except that the experimental curves are about 40 meV higher in energy than those predicted by the model. This seems to indicate that our modeling of the 3 ML Au barrier layer is oversimplified. In particular, assigning a bulk band structure to the entire width of such a thin Au barrier should not be expected to yield very accurate results. It does reflect the basic electronic structure of the Au barrier, however, giving the correct qualitative and approximate quantitative results. The measured gap of the avoided crossing at $x=14$ agrees very well with the theory.

Additional information can be gained from a study of

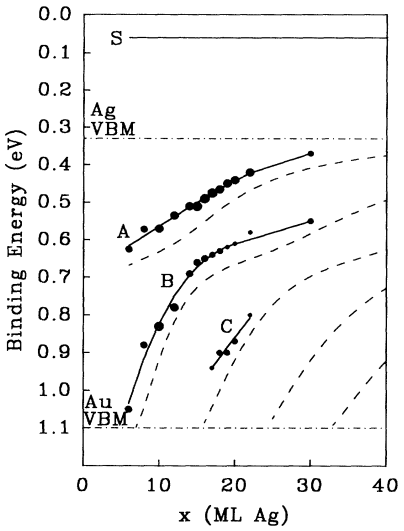

FIG. 3. Experimental binding energies (circles) for the double-quantum-well system Au(111)/Ag_8/Au_3/Ag_x as a function of outer well thickness x. Experimental uncertainty is less than 20 meV for states A and B, and about 40 meV for state C (see Fig. 2). The area of each circle is proportional to the photoemission intensity (due to the uncertainty, only five different intensity levels are used). The smooth solid curves labeled A-C are polynomial fits to the data and serve as a guide to the eye. The corresponding theoretical results from Fig. 1 are shown as dashed curves.

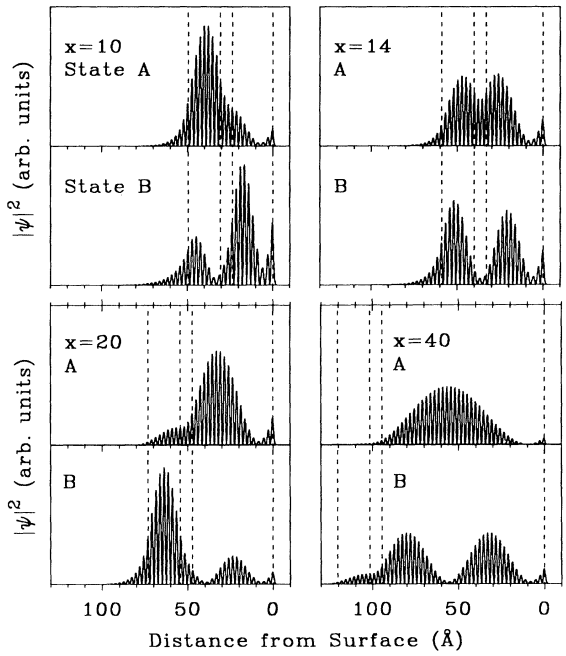

FIG. 4. Probability densities $|\psi|^2$ of states A and B for a few representative outer well thicknesses. All states are normalized and shown using the same vertical scale. The horizontal axis measures distance in Å from the surface. Vertical dashed lines indicate interfaces separating (from right to left): vacuum, x ML Ag outer well, 3 ML Au barrier, 8 ML Ag inner well, and Au(111) substrate.

the wave functions. The calculated probability density $|\psi|^2$ for a few representative cases is shown in Fig. 4. For $x=10$ ML, state A roughly corresponds to state I, and state B to state O_1, although significant mixing is already present. At $x=14$ ML, states I and O_1 are fully mixed. It is interesting to note that the higher energy state (A) has an antinode in its envelope function at the barrier, while the lower energy state (B) has a node, which differs from the standard result of a square well potential for an electron. This is a result of the "hole-like" dispersion of the Ag and Au sp band near the L point [2-4]. The states A and B continue to evolve as discussed earlier, until, at 40 ML, state A has evolved into state O_1, and state B has (almost) evolved into state O_2.

These calculated wave functions can be used to predict relative photoemission intensities when combined with a simple model of the photoemission process. Our model neglects the details of the final band structure, assuming simply that the photoemission intensity is a convolution of the initial state $|\psi|^2$ and the probability of escape, $\exp(-z/\lambda)$, where z is the distance from the crystal surface and λ is the photoelectron escape depth. The predicted photoemission intensities are indicated in Fig. 1 by the size of each circle. Since $\lambda=20$ Å is small compared to the double-quantum-well width (40-100 Å), almost none of the photoemission intensity is derived from electrons in the inner well. This explains the apparent disappearance of state B in the photoemission spectra near $x=20$ ML in Fig. 2. As can be seen in Fig. 4, state B has shifted mostly into the inner well, greatly reducing its photoemission intensity. Similar predictions can be made for the other cases. In particular, note that for large x, the photoemission intensity of all states, except the surface state, should slowly decrease as x is increased. This is because these states are distributed over increasingly larger depths, which causes a dilution of the wave function within the photoemission probing depth. When combined with the smaller energy spacing between states, this decreased intensity makes it harder to resolve the states as x is increased [2,5]. A comparison of the predicted and observed photoemission intensities (Figs. 1 and 3) shows that the principal qualitative features agree, namely, (a) state A's intensity remains fairly constant for x less than about 20 ML, after which it slowly decreases, and (b) state B's intensity decreases rapidly as it evolves away from state O_1 into mostly state I, and recovers somewhat as it further evolves into state O_2 at large x.

Thus, our experimental observation and theoretical prediction of the binding energies and photoemission intensities as functions of x show generally good agreement. The significant modification of the $E(x)$ dispersions in going from two independent quantum wells to a pair of

coupled quantum wells provides direct evidence for the electronic coupling through the Au barrier. In our model, the Hamiltonian of the system is not explicitly invoked; rather, it is embedded in the $E(k)$ dispersion relations and the wave functions for the Ag and Au valence bands. The electronic coupling between layers is determined by matching the wave functions. The boundary condition at one interface determines the phase shift of the wave functions, which in turn affects the matching of the wave functions at the next interface, and so on. If a perturbative approach is adopted, this translayer coupling is a higher order process. As mentioned earlier, the size of the gap due to the avoided crossing is twice the off-diagonal, effective coupling matrix element. Thus, this matrix element for a 3 ML Au barrier is on the order of 0.07 eV. This decays rather rapidly as the Au barrier thickness is increased, because the interaction is via nonpropagating (exponentially decaying) waves within the Au barrier [2,4]. It is interesting to note that if the coupling is via propagating waves, i.e., quantum-well states or resonances, a longer-range interaction with spatial structures can be expected (such as the periodic magnetic coupling in magnetic multilayer systems in which the magnetic alignment is just another manifestation of the electronic coupling, albeit spin polarized) [1,6].

In summary, this is an experimental study, supported by theory, of layer coupling effects in a prototypical multilayer system. The results provide a simple and intuitive example illustrating a basic form of electronic translayer coupling.

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