PHYSICAL REVIEW B VOLUME 50, NUMBER 12 15 SEPTEMBER 1994-II

Hybridization and the effective mass of quantum-well states in magnetic multilayers

P. D. Johnson, K. Garrison, and Q. Dong
Physics Department, Brookhaven National Laboratory, Upton, New York 11973

N. V. Smith
Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, California 94720

Dongqi Li, J. Mattson, J. Pearson, and S. D. Bader
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 22 June 1994)

Angle-resolved-photoemission studies of the dispersion of the quantum-well states in copper thin films deposited on a Co(001) substrate reveal that hybridization in the interface leads to a large increase in the effective mass of the electrons. These observations have implications for theories of the oscillatory exchange coupling in the related magnetic multilayers, particularly where Fermi-surface spanning vectors away from the center of the zone are invoked as in the case of the short-period oscillation in the Co/Cu(001) multilayers.

The potential technological applications for transition-metal multilayers have promoted a vigorous research activity.[1] A number of magnetic multilayer systems display an oscillatory exchange coupling between adjacent ferromagnetic layers dependent on the thickness of an intervening nonmagnetic layer.[2] Further, when antiferromagnetically coupled, a number of these systems show considerable enhancements in their magnetoresistance.[3] Several theories of the exchange coupling invoke the bulk band structure and associated Fermi-surface spanning vectors for the intervening layer.[4,5] Such theories often predict more than one period of oscillation for the coupling, reflecting additional spanning vectors away from the center of the zone. As an example, the Cu/Co(001) multilayer is predicted to have two periods of oscillation corresponding to spanning vectors at the center and neck of the characteristic Fermi surface "dog's bone."[4] These two periods have recently been observed in multilayers grown using molecular-beam-epitaxy techniques.[6] Interestingly, however, the second period of oscillation, the shorter period length, appears only to have been observed in the multilayers with thicker intervening layers.

It has been suggested that quantum-well states mediate the exchange coupling in these systems.[7,8] The presence of such states is a direct reflection of the finite thickness of the individual layers within the multilayer, i.e., the finite boundary conditions lead to a quantization of the electronic structure perpendicular to the layer. Quantum-well states observed in noble-metal thin films deposited on ferromagnetic substrates are highly spin polarized as a result of the hybridization in the interface between the overlayer and substrate.[9–11] This observation, together with the observation[12] that as a function of film thickness, the states move up to and through the Fermi level with a frequency identical to that found for the oscillatory exchange coupling lends support to the idea that they do indeed mediate the coupling in the associated multilayers.

Previous studies of the quantum-well states in the Cu/Co(001) system[11,12] have concentrated on those states observed at the center of the Brillouin zone. These states have been shown to be highly spin polarized and to cross the Fermi level with a periodicity of approximately 6 ML. This corresponds to the long period of oscillation observed in the related multilayers.[13] However, the short period of oscillation will, as noted above, involve states away from the center of the zone.[4] In terms of the electronic structure of bulk copper, the Fermi surface at the neck of the dog's bone will be sampled by bands or states that disperse upwards from the center of the zone with a free-electron-like effective mass.

In this paper we report a study as a function of film thickness of the dispersion of the quantum-well states away from the center of the zone in copper films deposited on a Co(001) substrate. We show that hybridization at the interface results in a large enhancement of the effective mass of the states in the thinner films. With increasing thickness, the effective mass reduces to that characterizing free-electron-like behavior. At around 8 ML, the bulk band structure of Cu again provides a realistic picture of the electronic structure of the film. These results provide an understanding of why the short period of magnetic coupling in the Cu/Co(001) multilayers does not develop until the copper spacer layer is thicker.

The experiments reported in this paper were carried out using the angle-resolving photoemission capability of the U5 beamline at the NSLS.[14] The sample cleanliness and crystallographic order were monitored using Auger electron spectroscopy and low-energy electron diffraction, respectively. The samples were prepared by first evaporating Co, typically 20 ML onto a Cu(001) substrate. The rate of evaporation was monitored with a quadrupole mass spectrometer. Copper films with thicknesses from 2 to 8 ML thick were subsequently deposited on the thick fcc Co film. With fixed incident photon energy, the electron spectrometer was moved away from the surface normal to record photoemission spectra corresponding to different parallel momenta in the surface Brillouin zone.

In Fig. 1 we show a representative series of photoemission spectra recorded as a function of the angle of emission from a 4-ML-thick copper film. The incident photon energy is 22.7 eV and the angle of incidence of 60° corresponds to

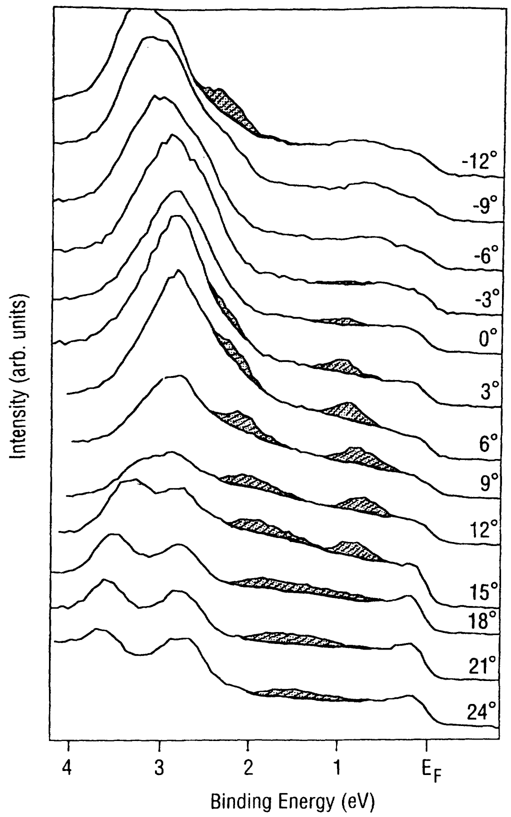

FIG. 1. Photoemission spectra recorded from a 4-ML-thick copper film as a function of the angle of emission as indicated. The incident photon energy is 22.7 eV and the angle of incidence of the light corresponds to p-polarized light. The quantum-well states are indicated by the hatched lines.

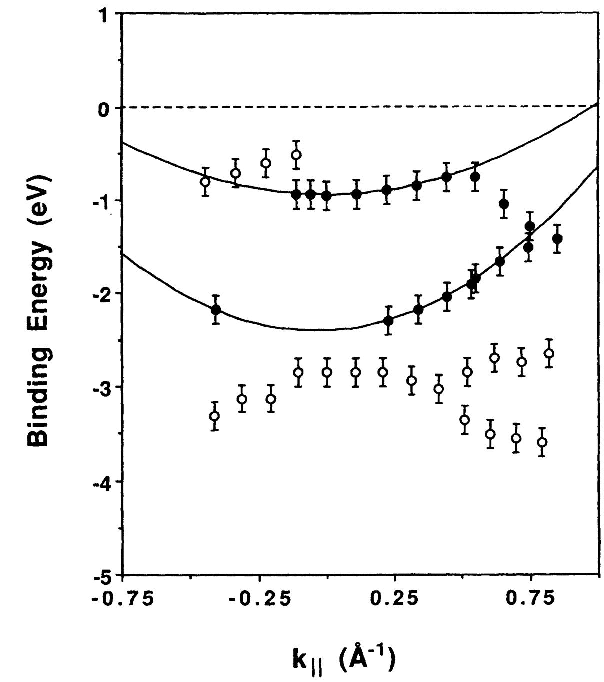

FIG. 2. Dispersion of the states observed in Fig. 1 plotted as a function of $k_{\|}$, the parallel component of momentum in the surface Brillouin zone. The quantum-well states are indicated by the filled circles; other states are indicated by open circles. The solid lines indicate the quadratic fits to the dispersion of the quantum-well states. The dashed line represents the Fermi level.

p-polarized light. The angle of emission is varied along the $\bar{\Gamma}\bar{X}$ azimuth. The peak at a binding energy of 0.9 eV in the spectrum recorded along the surface normal represents the quantum-well state that has been reported in several earlier studies.[10–12] As the angle of emission is increased, the state is observed to disperse upwards towards the Fermi level. The copper d bands are observed in the range from 2.5 to 4.0 eV binding energies. At larger angles, a second state emerges from these copper d bands and disperses towards the Fermi level with increasing emission angle. We again associate this state with the quantization of the allowed states in the k perpendicular direction. In the terminology of a phase analysis,[15] the first quantum-well state corresponds to the $\nu=1$ state, which for normal emission crosses the Fermi level at a film thickness of the order of 6 ML. Here the quantum number ν describing the wave function of the quantum-well state at any film thickness is the difference between the number of layers in the film and the number of nodes in the wave function. The second state corresponds to the $\nu=2$ quantum-well state, which crosses the Fermi level in normal emission at approximately 11 ML. Although not shown here, two states are also observed in spectra recorded from the 8-ML-thick copper film. In the latter case, the two states correspond to the $\nu=2$ and 3 quantum-well states.

In Fig. 2 we plot the dispersion as a function of $k_{\|}$ of the different peaks observed in Fig. 1. In order to plot the figure we assume that the work function of the film is identical to that measured for Cu(001) surface, i.e., 4.6 eV.[16] The figure clearly shows that the dispersion of the second quantum-well state is faster than the first. Further out in the zone in the vicinity of 9°–12° emission angle, the strong hybridization with the substrate reverses the dispersion of the first quantum-well state causing the two to merge. It is unclear that either state will cross the Fermi level. We also show in the figure the dispersion observed for the copper d bands.

By fitting the dispersion of the quantum-well states with a quadratic form we obtain a measure of the effective mass m^* of the electrons as defined by $E=\hbar^2k_{\|}^2/2m^*$. In Fig. 3 we plot these effective masses as a function of the copper film thickness. For the 4- and 8-ML-thick films the figure shows the effective masses obtained from both observed quantum-well states. The effective mass plotted for the 6-ML film represents a single set of measurements of the deeper-lying quantum-well state. It is not possible to obtain an effective mass from the state immediately below the Fermi level. For any given thickness, the spread in the range of effective masses reflects the difficulty of obtaining an accurate fit when matrix element effects result in the quantum-well states being observed with strong intensity only in the direction of the incident-light polarization vector. Thus only half of the "picture" is observed experimentally. However the trend is very clear. *As the films become thinner, hybridization in the interface results in a large enhancement of the effective mass in the plane of the film.* The figure clearly shows that as the films become thicker, the effective mass

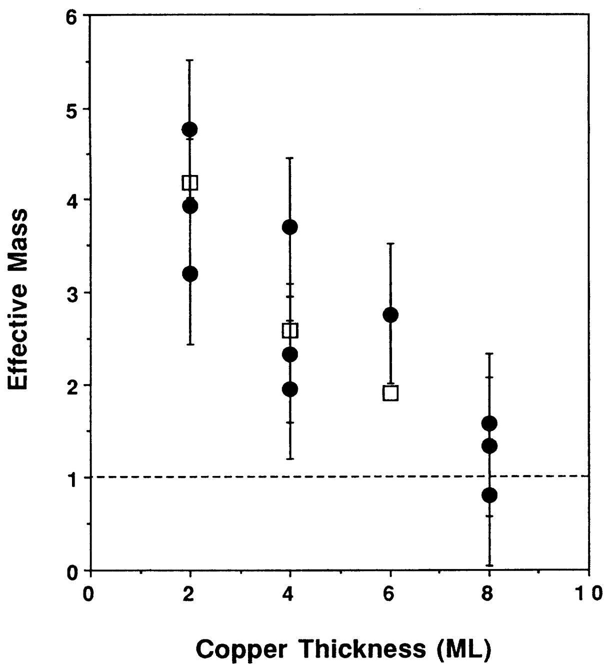

FIG. 3. Plot of the fitted effective masses of the quantum-well states as a function of the copper film thickness in atomic layers. The solid circles indicate the fits to the experimental data; the open squares indicate the results of tight-binding calculations of the effective masses. The dashed line represents the free-electron mass.

approaches the free-electron value that would characterize an isolated copper slab. Indeed, such a free-electron-like dispersion has been calculated for these states in a linear combination of atomic orbital calculation of copper slabs of different thicknesses.[17] For the thicker films, band-structure effects may produce in-plane effective-mass variation of the order of 10%.[18]

The increase in the effective mass in the thinner films directly reflects the degree of hybridization with the substrate *d* bands. As the film becomes thicker, the dispersion is influenced more by the electronic properties of the copper. This effect may be reproduced with tight-binding analysis as shown in Fig. 3. Using the analysis that we have previously used to examine the spin-polarization properties of the quantum-well states,[10] we find that calculations of the effective mass provide a more sensitive determination of the appropriate parameters than calculations of the binding energies at the center of the zone. Thus, in order to get reasonable agreement with the observed effective masses, it was necessary to adjust the level of interaction in the interface. This was achieved by simply increasing the Co-Cu spacing. This has little effect on the binding energies predicted at the center of the zone when compared with our previous calculations. Having adjusted the interfacial parameters to obtain the effective mass for the 2-ML-thick film, other than increasing the number of copper layers, no further adjustment was required to calculate the effective masses for the thicker films. We note in passing that a tight-binding calculation of an isolated 2-ML-thick copper film reproduces the free-electron-like dispersion found in the thicker slab calculation.[17] This supports the idea that the enhancement reflects the interface effects rather than a thin-film effect.

The increase in the effective mass of the quantum-well states is a clear indication that hybridization and interfacial effects cannot be ignored in any theoretical description of the coupling in multilayers with thin intervening layers. These effects may well modify the coupling and indeed, as noted earlier, experimental studies of the Cu/Co(001) multilayers appear to indicate the absence of the short-period oscillation in the multilayers with thinner intervening layers.[6] We would further suggest that it may also be appropriate to consider the enhanced effective masses of these states in any modeling of the transport properties of these systems.

This work was supported in part by the Department of Energy under Contracts Nos. DE-AC02-76CH00016, DE-AC03-76SF0098, and W-31-109-ENG-38 and in part by the Office of Naval Research under Contract No. N-00014-94-F-0085.

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