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G. Mankey – University of Alabama

et al.

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# Quantum size effects in ultrathin Cu(100) films

G. J. Mankey and R. F. Willis

*Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802*

J. E. Ortega

*Departamento de Física de la Materia Condensada, C-III, Universidad Autónoma de Madrid, Cantoblanco, E-28049, Madrid*

F. J. Himpsel

*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*

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We report an angle resolved photoemission study of quantum size effects observed in the electronic structure of pseudomorphic Cu(100) films. The 3*d* band of a one-layer film exhibits an 80% reduction in its perpendicular dispersion and a 10% reduction in its parallel dispersion. The perpendicular dispersion of the 3*d* band evolves rapidly with increasing film thickness, since the 3*d* electrons are strongly localized on the ion cores. Quantum-well resonances are produced due to the discretization of the perpendicular wave vector in the *s,p* band. They produce oscillations in the Fermi level intensity as they disperse through it when the film thickness is increased. The observed oscillation period of approximately six layers matches that of oscillations in the magnetic exchange coupling between ferromagnetic Co films separated by Cu spacer layers. The connection of the quantum-well states to bulk electronic structure is determined by comparing oscillation amplitudes for two different photon energies.

## I. INTRODUCTION

Advances in molecular beam epitaxy and techniques have made possible the production and characterization of ultrathin metallic films of atomic dimension. High-quality epitaxial films can be produced by vapor deposition in an ultrahigh vacuum environment on suitably prepared substrates. Here photoemission measurements will be presented for ultrathin Cu films deposited on pseudomorphic fcc Co(100). This fcc Co(100) film is an ideal substrate for studying the evolution of the electronic structure of Cu(100) overlayers, because it has the same lattice constant as bulk Cu and the 3*d* bands of the Co are well separated in energy from the 3*d* bands of the Cu film. We searched for quantum size effects in these films. They are observed as discrete transitions in the *s,p* band and as modulations in the photoemission intensity at the Fermi energy extending over many atomic layers.

## II. EXPERIMENT

The observation of surface-state spectral features associated with the 3*d* band and quantum-well resonances in the *s,p* band requires coherent electron scattering within highly uniform films. Our Cu(100) substrate preparation procedure and film thickness calibration techniques have been reported earlier.<sup>1</sup> A 12 monolayer (ML) Co film was deposited on this substrate to produce a well-ordered pseudomorphic fcc Co(100) substrate. The Co films were grown at room temperature in a vacuum in the low 10<sup>-10</sup> mbar range and annealed to 150 °C to improve long range order. These films exhibited a (1×1) low energy electron diffraction (LEED) pattern with sharp integral order spots. Cu films were then deposited on this Co(100) substrate at room temperature. Photoemission spectra were recorded at one-layer intervals for Cu(100) overlayers. For all photoemission measurements presented here, unpolarized light was incident at an angle of

45° from the surface normal in the  $\Gamma\Delta M$  mirror plane. In addition to measurements at discrete film thicknesses, continuous measurements of the Fermi level intensity were made while depositing Cu from a separate source in the analysis chamber. This allows us to look for fine structure in the intensity oscillations of the *s,p* band, which are produced by quantum size effects.

## III. RESULTS

Theoretical calculations predict both a narrowing of the 3*d* band and an upward shift in its mean energy for an isolated layer of Cu(100).<sup>2</sup> A plot of the band structure for bulk Cu(100), along with the energies of the transitions observed for photoemission with three photon energies produced with a laboratory resonance lamp (Vacuum Generators UV Lamp), is shown in Fig. 1. The photon energies are 21.22 eV for He I, 16.85 eV for Ne I, and 11.83 eV for Ar I. The empirical free-electron-like final band<sup>3</sup> is shifted down by the corresponding photon energy to locate the positions of the direct transitions. The transitions observed for He I correlate well with the 3*d*-like  $\Delta_2$  and  $\Delta_5$  bands, and the *s,p,d* hybridized  $\Delta_1$  band. For Ne I, a single peak is observed due to the overlapping energy bands. For Ar I, two distinct transitions are seen from the 3*d*-like  $\Delta_5$  band and the *s,p*-like  $\Delta_1$  band. For the one-layer film, the energies of the most intense transition is plotted in each case. This feature corresponds to the  $\Delta_5$  band of bulk Cu(100). This band exhibits a dispersion of 20% of the bulk 3*d* band dispersion and an upward shift of 0.47 eV in the mean energy over the range of photon energies measured. No perpendicular dispersion is expected for a truly two-dimensional layer. The upward shift and nonzero dispersion could be an indication of some hybridization of the Cu 3*d* band with the Co 3*d* band.

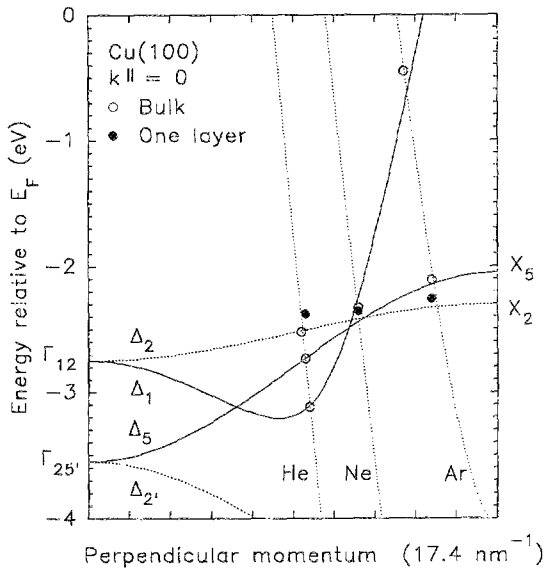


FIG. 1. Band structure of Cu(100) and observed transitions for bulk Cu(100) (open circles) and a one-layer Cu(100) film (filled circles). The observed transitions are extracted from spectra taken with  $h\nu=21.22$  eV for He I,  $h\nu=16.85$  eV for Ne I, and  $h\nu=11.83$  eV for Ar I.

Normal emission photoemission spectra recorded at one-layer intervals are shown in Fig. 2. The integrated 3d band intensity (see the inset) follows an exponential growth law for increasing Cu thickness with a measure of the sampling depth of the photoemission experiment given by 4.2 layers. The work function for films greater than one-layer thick is within 0.05 eV of the value measured for bulk Cu(100), indicating the one-layer film completely wets the Co(100) surface. A close inspection of the spectra reveals that much of the change in the 3d related features occurs over the first few

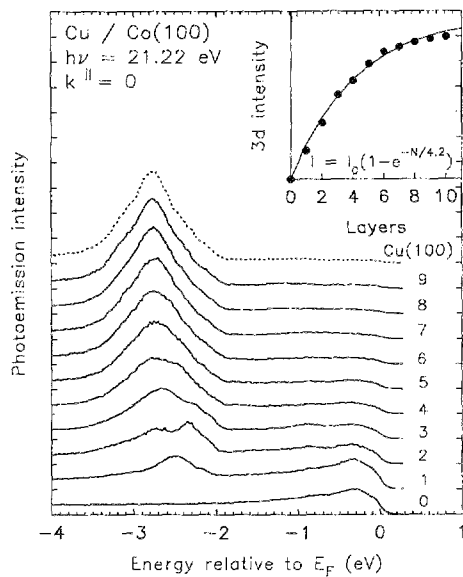


FIG. 2. Normal emission photoemission spectra for Cu layers deposited on Co(100) as a function of film thickness. The inset shows the evolution of the integrated 3d band intensity with increasing film thickness.

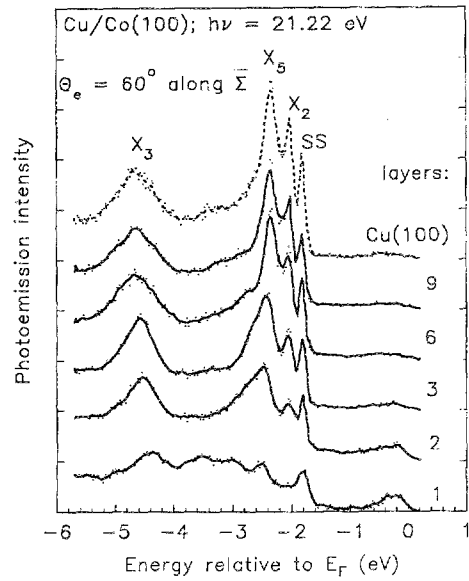


FIG. 3. Photoemission spectra taken near the  $\bar{M}$  point in the surface Brillouin zone as a function of film thickness. The top spectrum (dashed line) is bulk Cu(100). Only a slight narrowing of the parallel dispersion of the 3d band is observed for the one-layer film.

atomic layers, with the spectrum from the five-layer film being nearly identical to that of bulk Cu(100).

The development of the parallel dispersion of the 3d band was determined by comparing spectra taken near the  $\bar{M}$  point for films of varying thickness, Fig. 3. The main peaks in the spectra correspond to the  $X_3$ ,  $X_2$ , and  $X_5$  symmetry points, and the feature labeled SS corresponds to the Tamm surface state derived from the  $\Delta_5$  band.<sup>4</sup> At the X point in the Brillouin zone, the total bandwidth in the parallel direction is measured. The energy of the  $X_3$  critical point shifts by 0.35 eV to higher energy for the one-layer film. This is accompanied by a 0.05 eV shift to higher energy of the Tamm surface state. These shifts indicate the 3d band is narrowed by  $0.3 \pm 0.1$  eV for the monolayer film [10% of the total bandwidth of 3.12 eV for bulk Cu(100)]. This observation is to be compared to by photoemission measurements of Cu layers on Ni(100), which showed no reduction in parallel dispersion and an upward shift of 0.4 eV.<sup>5</sup> The small difference in these observations reflects the 3% lattice compression of Cu on Ni(100).

The Tamm surface state is observed in all the thin film spectra. This is an indication of well-ordered films, since disordered films do not exhibit sharp surface states. Further, since it is derived from the  $\Delta_5$  band, the 1 ML film exhibits a less well-defined peak at the energy corresponding to the  $X_5$  critical point. For the 2 ML film, the intensities of the transitions from the  $X_5$  critical point and the Tamm surface state are nearly equal, which shows the potential experienced by the underlying Cu layer is nearly the same as the potential in the bulk material. These measurements show the energies of the 3d bands do not display large chemical shifts associated with the binding of the interface layer to the Co(100) substrate. This is due to the short screening length of the electrons in metals. The dispersion of the s,p band is more

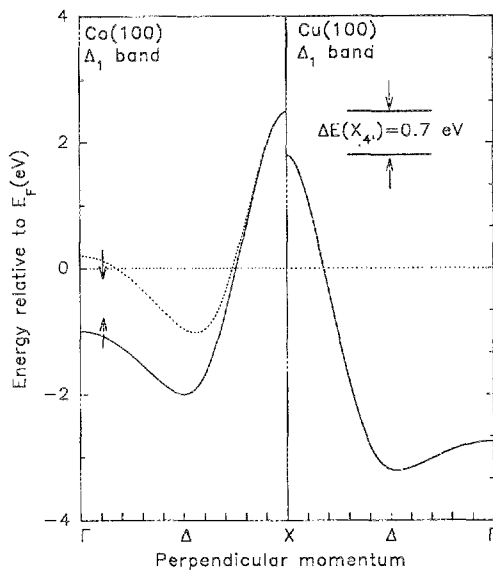


FIG. 4.  $\Delta_1$  band dispersion for Co(100) and Cu(100) along the direction perpendicular to the interface. The bands change from  $3d$ -like at  $\Gamma$  to  $s, p$ -like at  $X$ . The spin polarization of the Co bands is indicated by the up and down arrows. The band mismatch at  $X$  gives electron reflection at the interface.

sensitive to the difference in inner potentials of the Cu film and Co substrate, and this produces quantum well oscillations in the  $s, p$  band.

Quantum-well states are observed in Cu films deposited on Co(100).<sup>6</sup> These states derived from the band mismatch at the zone boundary. The relevant band gap here is the  $X_{4'} - X_1$  energy gap at the fcc zone boundary, at which the phase of the Bloch wave varies from zero at the antibonding  $p_z$ -like  $X_{4'}$  point to  $\pi$  at the bonding  $s$ -like  $X_1$  point. Using photoemission and inverse photoemission, we have accurately determined the energies of the  $X_{4'}$  and  $X_1$  critical points at 1.8 and 7.8 eV above  $E_F$  for fcc Cu(100) and at 2.5 and 9.6 eV for pseudomorphic fcc Co(100).<sup>3</sup> This produces a band offset of  $\Delta E(X_{4'}) = 0.7$  eV for the  $p_z$ -like lower branch, which is shown in Fig. 4, and  $\Delta E(X_1) = 1.8$  eV for the  $s$ -like upper branch along the direction normal to the film/substrate interface. The band offset is a measure of the step in the inner potential at the interface.

Quantum-well states are observed in inverse photoemission spectra and secondary electron distributions at energies above  $E_F$  and in photoemission spectra at energies below  $E_F$ . Strictly speaking, quantum-well stationary states within the Cu overlayer exist only within the  $X_{4'} - X_1$  energy gap of the Co substrate for which there are no states available in the  $k^\perp$  direction. However, since the energy-dependent reflection coefficients at the film/substrate interface remains finite for energies outside the gap, these states extend down through  $E_F$ , due to partial (rather than total) reflection. Their energy dispersion with increasing film thickness can be modeled using an envelope function formalism developed to explain similar effects in semiconductor superlattices.<sup>7</sup>

The wave function in the quantum well is described as a rapidly oscillating carrier wave Bloch function modulated by

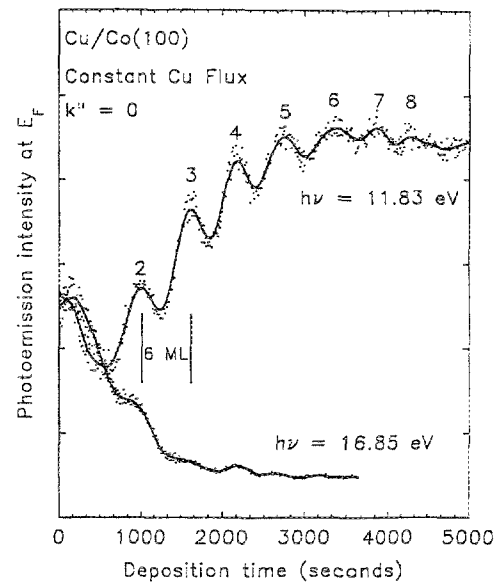


FIG. 5. Normal emission Fermi level intensity versus film thickness for Cu deposited on Co(100) at photon energies corresponding to Ne I ( $h\nu = 16.85$  eV) and Ar I ( $h\nu = 11.83$  eV). Strong oscillations are observed only in the vicinity of a bulk  $s, p$  band transition (Fig. 1). The period in each case is approximately six layers.

a slowly varying envelope function with total wave vector:

$$k_{\text{tot}}(E) = k_{\text{edge}} - k_{\text{env}}(E). \quad (1)$$

In the absence of any major changes in the band structure due to bonding at the interface, the total wave vector will follow the dispersion of the bulk bands, and  $k_{\text{env}}(E)$  is determined by Eq. (1). The envelope function is analogous to the Fabry-Pérot etalon analog in optics, in which the electrons or holes are partially reflected at the substrate/film and film/vacuum interfaces, interfering constructively to produce resonant states.<sup>8</sup> Constructive interference at a particular energy,  $E$ , occurs at film thicknesses  $d_n(E)$  that satisfy the quantization condition:

$$2k_{\text{env}}(E)d_n(E) + \phi(E) = 2[k_{\text{edge}} - k_{\text{tot}}(E)]d_n(E) + \phi(E) = 2\pi(n-1), \quad (2)$$

where  $n$  is a positive integer. For a given  $n$ , a change in the thickness  $d_n(E)$  is accompanied by a corresponding change in  $k_{\text{env}}(E)$ , i.e., the  $n$ th quantum-well state will have a thickness-dependent energy.

For a particular energy, the overall phase shift is constant and constructive interference will occur with a period equal to half that of the envelope function  $p(E) = \lambda_{\text{env}}(E)/2$ , with wave vector  $k_{\text{env}}(E) = \pi/p(E)$ . At the Fermi energy, this has an interesting consequence. There, the resonance states cross the Fermi level and the phase matching condition is given by  $k_{\text{env}}(E_F) = k_{\text{edge}} - k(E_F)$ . For Cu(100) at  $X$ ,  $k_{\text{edge}} = \pi/a$  and  $k(E_F) = 0.827 k_{\text{edge}}$ , so the photocurrent at the Fermi energy will exhibit periodic oscillations with period  $p(E_F) = 5.78(a/2)$ , where  $a/2 = 1$  layer = 1.8 Å. That these are indeed observed is shown in Fig. 5. The period of the intensity oscillations at  $E_F$  for Cu(100) corresponds to the modulation wave envelope function periodicity of six layers.

The oscillations are much weaker for Ne I ( $h\nu=16.85$  eV), which shows that a strong modulation is observed only in the vicinity of the bulk  $s,p$  band.

The period of these oscillations matches those observed in the oscillatory ferromagnetic (FM)/antiferromagnetic (AFM) coupling between Co layers as a function of Cu thickness,<sup>9</sup> which suggests that these states are the origin of the magnetic coupling through the nonmagnetic layers. Here, states within  $kT_c$  of  $E_F$ , where  $T_c$  is the magnetic transition temperature, contribute the most to the magnetic coupling. The spin polarization of the quantum-well resonances has been determined to be of minority character,<sup>10</sup> which shows they transmit spin information via polarization of the  $s,p$  band of the Cu film. How they relate to the Fermi surface of the spacer layer has recently been described theoretically.<sup>11</sup> The magnetic interaction integrates over  $k^{\parallel}$  (i.e., the whole of the Fermi surface must be considered), with the extremal points of the Fermi surface producing both long and short period oscillations.

#### IV. SUMMARY

We have measured quantum size effects in the electronic structure of ultrathin Cu(100) films. The  $3d$  band for one layer exhibits an 80% reduction in its perpendicular dispersion, as compared to bulk Cu(100) over the range of photon energies used. Since the  $3d$  band is much narrower than the  $s,p$  band, this band becomes bulklike over the first few atomic layers. The parallel dispersion of the  $3d$  band is re-

duced by only 10% for a one-layer film. Quantum size effects in the  $s,p$  band are seen as oscillations in the photoemission intensity at the Fermi level. These oscillations persist up to film thicknesses of 50 layers with a period of six monolayers, determined by the geometry of the Fermi surface.

#### ACKNOWLEDGMENT

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