Quantum Well States and Short Period Oscillations of the Density of States at the Fermi Level in Cu Films Grown on fcc Co(100)

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Quantum well states are observed around the "neck" of the Fermi surface in Cu films grown on magnetic fcc Co(100) substrates, using high-resolution angle-resolved photoemission. The observation is only possible with an abrupt, nonreacted Cu/Co interface, which is produced by low temperature deposition of the first Cu layer. The analysis of the spectra gives a periodic crossing of the Fermi level of $\sim$ 2.6 atomic layers, the same short magnetic coupling period obtained in Co/Cu/Co trilayers, and also the same value predicted by the theory. This is a strong confirmation of the role of quantum well states as mediators of magnetic coupling in superlattices. [S0031-9007(96)01428-7]

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The oscillatory exchange coupling between magnetic layers separated by a nonmagnetic metal thin film spacer [1] created in past years a widespread interest, due both to the potential applications and to the unexpected periodicities observed. The discovery of quantum well (QW) states and the related oscillations at the Fermi level [2], as well as their spin-polarized character [3], in thin noble metal (Cu, Ag) films deposited on ferromagnets (Co, Fe) suggested a direct connection between these states and magnetic coupling in superlattices. The role of QW states as mediators of magnetic coupling was already predicted in the early theoretical model of Edwards *et al.* [4], who directly linked the oscillatory coupling to the periodic change in the spectral density of the spacer, which is considered as a quantum well of varying thickness. The QW model, such as the Ruderman-Kittel-Kasuya-Yosida-(RKKY-) like model [5], predicts magnetic coupling periods dictated by the shape of the Fermi surface of the spacer; i.e., in the QW model only the oscillatory density of states at the Fermi surface extrema is relevant to magnetic coupling. In the case of the well-known Co/Cu/Co(100) system the two extreme points of the Cu Fermi surface, namely, the "neck" and the "belly," give rise in the QW model to two different magnetic coupling periods of 2.6 and 5.7 monolayers (ML), respectively. These are indeed close to the periodicities found in magnetic measurements: from 5.5 [6] to 8 ML [7] for the long period and 2.6 ML [7] for the short period. On the other hand, the long period oscillation of the density of states at E_F is the one observed in inverse and direct angle-resolved photoemission spectroscopy (ARUPS) measurements (5.9 ML) [2], since these were taken under normal emission geometry, i.e., probing states at the belly of the Fermi surface. Therefore, in order to definitely probe the connection between photoemission experiments, the QW-model predictions, and the observed oscillatory magnetic coupling, it is necessary to demonstrate the existence of QW states and the related short period oscillations at the neck. This is done in this Letter for Cu films deposited on fcc Co(100), i.e., we present the experimental evidence for QW states at the neck of the Cu Fermi surface which lead to short period oscillations of the density of states at E_F. Such an observation is only possible with a nonreacted, abrupt Cu-Co interface, which is produced by depositing the first Cu layer at low temperature.

ARUPS experiments were performed at the high-resolution VUV photoemission beam line of the synchrotron radiation laboratory ELETTRA at Trieste (Italy), with a total energy resolution of 40 meV and an angular resolution of better than $\pm 1°$. The polarization of the synchrotron light was set to p-like (70° incidence with respect to the surface normal) in order to enhance sensitivity to Δ_1-symmetry initial states. To normalize the photoemission spectra, we registered also the photon flux with a Au grid that intercepts the beam before it enters the chamber. Both Co and Cu were evaporated from electron-beam-heated sources, with a deposition rate of $\sim$ 1 Å/min. A fcc Co(100) film (10 ML) was grown at 300 K (RT) on top of a Cu(100) single crystal, which had followed a mechanical and electrochemical polishing treatment prior to the *in situ* sputter-annealing cycles [2]. On top of the Co film, the deposition of the first Cu layer was done at 100 K (LT), and it was immediately annealed to RT to provide a good surface diffusion of the Cu layer. Subsequent layers were deposited at RT. The LT deposition of the first layer is needed to prevent mixing at the interface, which can damp or even "wash out" QW features in the valence band [8].

The two different measurement geometries used in this work are schematized in Fig. 1. The thick arrows represent the initial state wave vector of Fermi level electrons at the two extrema of the dog bone, whereas thin arrows

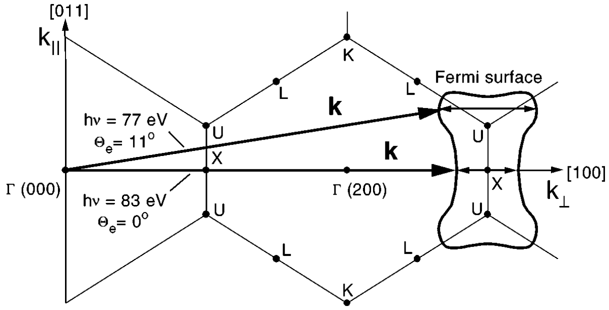

FIG. 1. Photoemission geometry to detect states at the belly ($h\nu = 83$ eV, normal emission) and at the neck ($h\nu = 77$ eV, 11° off-normal emission) of the Fermi surface of Cu.

are the Fermi surface spanning vectors whose magnitude determines the two different oscillation periods [9]. In photoemission experiments, vertical transitions to these two extreme points of the Fermi surface are possible in the conditions indicated in Fig. 1. Under normal emission geometry with angular resolution, the Fermi level intensity is primarily due to states at the belly (thinnest part of the dog bone). Such an intensity is maximized with $h\nu =$ 83 eV, i.e., by selecting vertical transitions from E_F. To reach the neck (or "head" of the dog bone) it is necessary to change the photon energy and move the emission angle away from the normal direction [100] towards the [011] direction in the bulk Brillouin zone (or the $\overline{\Gamma}\,\overline{X}$ direction in the surface Brillouin zone). Around the nominal value for the neck ($k_{||} = 0.87$ Å^{-1} along [011]), we have maximized the Fermi level intensity by slightly moving both the photon energy and the emission angle, obtaining the conditions indicated in Fig. 1, i.e., $h\nu =$ 77 eV and $\theta_e = 11°$. This gives a fixed parallel momentum $k_{||} = [(2m^*/\hbar^2)E_{\mathrm{kin}}]^{1/2} \sin\theta_e = 0.8$ Å^{-1} along [011] for electrons at E_F.

In Fig. 2 we display the valence band region of the photoemission spectra obtained under normal emission. At this energy range, only s, p-like, Δ_1 states from Cu contribute to the spectrum. A first coverage calibration was obtained with a quartz microbalance. However, the exact number of Cu layers given in Fig. 2 is obtained by adjusting the periodic oscillations of the intensity at E_F to the expected periodicity of 5.8 layers [10]. Such a periodic oscillation is shown in the top panel of the figure. The thickness-dependent modulation of the valence band in Fig. 2 is expected for a bulk band which is being discretized in the direction perpendicular to the film. Because of the angular resolution, we are observing the discretization of the s, p-like band along the ΓX direction. The bumps can also be viewed as emission from QW states (numbered from 2 to 9) confined in the Cu film, whose position and number depend on the thickness. In fact, by increasing the number of layers, the peaks of Fig. 2 appear to move to the right side of the spectrum, crossing the Fermi level and leading to the periodic changes in

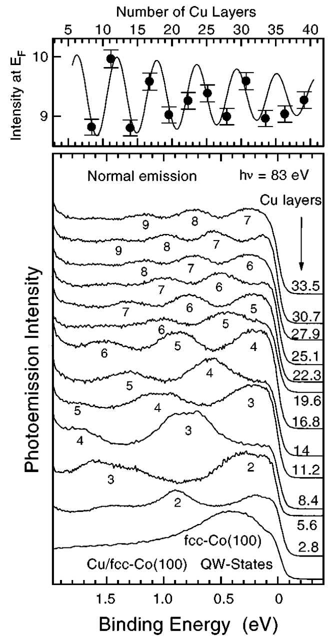

FIG. 2. Quantum well modulations (numbered from 2 to 9) in the valence band of a Cu film of increasing thickness near the belly of the Fermi surface (bottom). The Fermi level crossing of the QW states produces the long period (5.8 ML, 1.8 Å each) oscillation in the density of states at E_F (top).

the intensity shown in the top panel of the figure. The intensity at E_F is measured directly from the spectra, but it is normalized to the photon flux and also to the total intensity of the corresponding spectrum, which is found to change periodically as a function of Cu thickness. Such a variation is believed to be a sign of quantization of the photoemission final state [11]. The normalized-intensity data points are then fitted with a sinusoidlike function, with the period and the phase as fitting parameters. As a check to the fit, we can observe that the maxima always correspond to QW states crossing E_F in the spectra below. A small attenuation is needed for a correct fitting. This is also inferred from the spectra, where the QW modulations are damped for the thicker film. When we compare with a RT-deposited interface the QW states in Fig. 2 appear better defined [11]. On the other hand, we observe in Fig. 2 how the emission from the Co film underneath is almost attenuated with the first evaporation of 2.8 ML. In contrast, with a RT-deposited interface one needs about 6 ML of Cu to shade the valence band emission of Co [2]. This is an indication of the presence of a Cu-Co mixed layer at the interface during RT growth. Therefore mixing at the interface leads to the attenuation of the QW features, as also observed for rough (stepped) interfaces [12]. In the low-coverage spectra of Fig. 2 the QW states appear wider. Such an effect can be due to emission from areas with different thicknesses (at incomplete layer coverages), but also to the presence of spin-split components. We will discuss this issue elsewhere [11].

In Fig. 3 we show the valence band spectra for the same film of Fig. 2, but taken around the neck of the Fermi surface, as explained in Fig. 1. Angular resolution and parallel momentum conservation restrict us to a fixed value of $k_{\|}$ (~ 0.8 Å^{-1}), and hence for the energy range shown in Fig. 3 the emission is due to a portion of the s, p-like band similar to the one probed in normal emission (see this band in Fig. 4 of Ref. [13]). The valence band spectra in Fig. 3 are again strongly thickness dependent, indicating quantization of the electronic structure around the neck [14]. As in normal emission, the spectra also display total intensity variations, related to the quantization of the final state [11]. At the lowest coverages shown in Fig. 3 the spectra appear clearly modulated by QW features (numbers and tick marks), but in contrast to Fig. 2 the number of quantized states per energy interval is higher. The numbering of the states given in Fig. 3 is consistent with the analysis developed further below. The increased density of QW states hinders their visualization at higher coverages, but, as a sign of quantization, we can still detect big changes in the overall shape of the spectra. The number of QW states at a given thickness can be

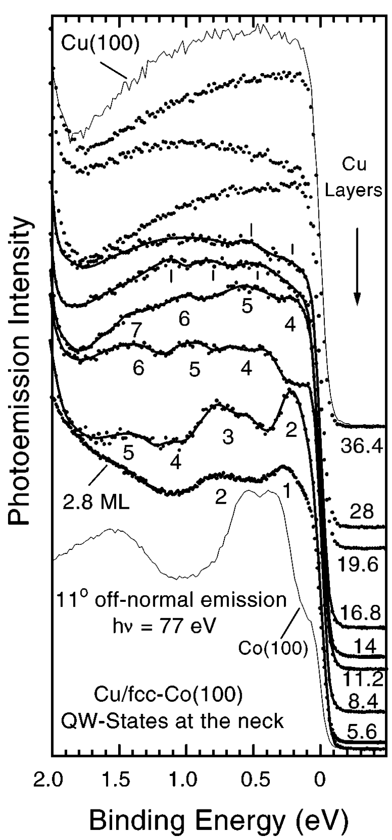

FIG. 3. Valence band photoemission spectra for the same Cu film as Fig. 2, but taken around the neck of the Fermi surface. The thick solid lines are guides to the eye. The spectra are thickness dependent, as expected for a quantized valence band, also for the thicker films. The typical QW features are observable only at lower thicknesses, but the overall shape displays big changes still at higher coverages.

calculated using the quantization formula [2]

$$d = [n - \Delta\phi(E)]/[1 - k_{\perp}(E)], \qquad (1)$$

where n is an integer, d is the thickness (in ML), $\Delta\phi(E)$ the energy-dependent total phase shift for the reflection of the electron waves at both sides of the film (in units of π), and $k_{\perp}(E)$ the bulk band dispersion in units of $2\pi/a$. Since the s, p-band portion tested here has basically the same dispersion as the band along ΓX [13], the shorter distance between states found in Fig. 3 is due to a faster energy variation of the phase for the reflection at the interface. This is what we expect close to the edge of a band gap [15], like the one opened up at about 0.6 eV below E_F for minority-spin electrons in the Co band structure around the neck [13]. We have to note that the energy dependence of the phase shift will not affect the oscillation periodicities of the density of states with thickness, which are strictly given by the inverse of $1 - k_{\perp}(E)$ [2].

A structure plot containing all the QW features of the spectra of Fig. 3 is displayed in the top panel of Fig. 4. In a first approximation, we can make a linear fit to the energy shift as a function of thickness for the same QW state. Indeed the relative variation of the denominator in Eq. (1) within the energy range here considered is very small. On the other hand, the phase shift can be assumed to have a linear dependence in energy [2], and hence the data points for different QW states in the structure plot are fitted with straight lines. The different crossing points at the Fermi level give the periodic oscillation of the intensity. We obtain a value of 2.6 ± 0.3 ML [16]. This is the same short periodicity obtained in magnetic measurements [7] and predicted either in RKKY-like models or in the QW theory for magnetic coupling [5,9,13]. This result is also consistent with the intensity plot in the lower part of Fig. 4. Here we represent the normalized photoemission intensity (dots) at E_F as a function of thickness. The evaporation rate allows us to observe the short periodic oscillation through a beating frequency. In fact, we notice that the intensity at E_F passes through maxima and minima every 14–19 ML. This is directly observed in the corresponding shape of the spectra of Fig. 3, especially for thicker films. Such a result indicates that we are sampling the short period oscillation with a close, but different, periodicity. The thick line represents the beating points of a short periodic oscillation (dotted lines) with the sampling frequency (i.e., the evaporation rate). The best fit is obtained for a period of 2.45 ML, which is within the error range of the period obtained from the analysis of the structure plot [17].

In summary, we present evidence for quantization of the electronic structure around the neck of the Fermi surface in Cu films deposited in Co(100). The observation is only possible with nonreacted interfaces, obtained by LT deposition of the Cu contact layer. The effect of the interface reactivity is to attenuate the QW states. This

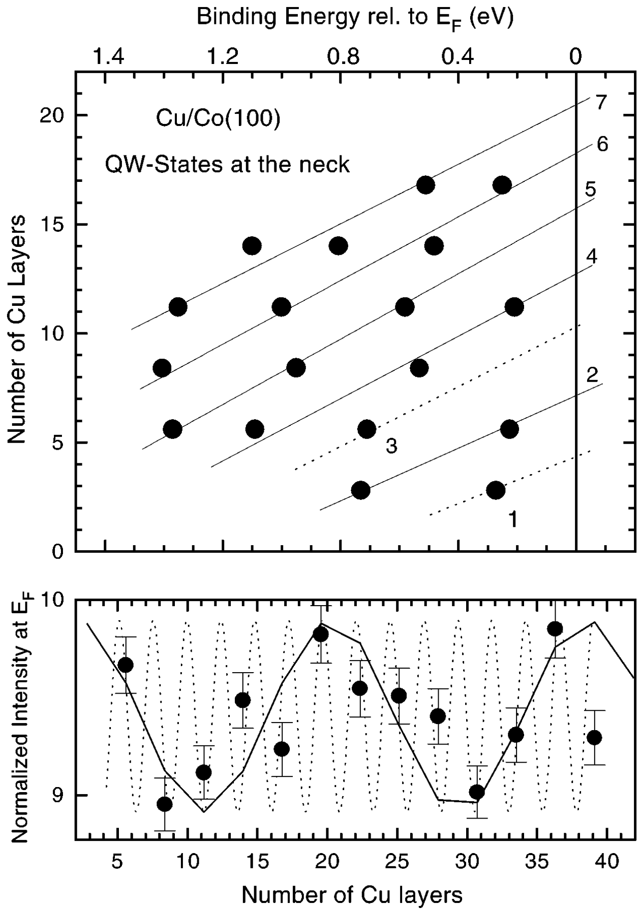

FIG. 4. Structure plot for the QW states of Fig. 3 (top). The linear fit to the different states is extrapolated to E_F, where a periodic crossing of states every 2.6 ± 0.3 ML (1.8 Å each) is obtained. For $n = 1$ and $n = 3$ two parallel crossing lines are estimated (dotted lines). In the bottom, the data points represent the photoemission intensity measured at E_F in the spectra of Fig. 3. The maxima and minima approximately follow the thick line, which represents the beating points for a short period oscillation (2.45 ML, dotted line) and the sampling frequency (2.8 ML).

is even more critical for shorter periodicities, and this explains why QW states at the neck were not previously found in RT-grown films [18]. The analysis of our QW-state data gives a short period oscillation of the density of states at the neck of about 2.6 ML, in accordance with QW theory and magnetic measurements. We have to note that QW states at the neck and their related short period oscillations at E_F have been found to have a major role in magnetic coupling, even more important than states at the belly [13]. Here we present experimental evidence of their existence.

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[1] S. S. P. Parkin *et al.*, Phys. Rev. Lett. **66**, 2152 (1991).
[2] J. E. Ortega and F. J. Himpsel, Phys. Rev. Lett. **69**, 844 (1992); J. E. Ortega *et al.*, Phys. Rev. B **47**, 1540 (1993).
[3] N. B. Brookes *et al.*, Phys. Rev. Lett. **67**, 354 (1991); C. Carbone *et al.*, Phys. Rev. Lett. **71**, 2805 (1993); K. Garrison *et al.*, Phys. Rev. Lett. **71**, 2801 (1993).
[4] D. M. Edwards *et al.*, Phys. Rev. Lett. **67**, 493 (1991).
[5] P. Bruno and C. Chappert, Phys. Rev. Lett. **67**, 1602 (1991).
[6] Z. Q. Qiu *et al.*, Phys. Rev. B **46**, 8659 (1992).
[7] W. Weber *et al.*, Europhys. Lett. **31**, 491 (1995).
[8] J. Kudrnovský *et al.*, Phys. Rev. B **53**, 5125 (1996).
[9] M. D. Stiles, Phys. Rev. B **48**, 7238 (1993).
[10] Here we take the k_F value from de Haas–van Alphen data of P. T. Coleridge and I. M. Templeton, Phys. Rev. B **25**, 7818 (1982).
[11] E. G. Michel *et al.* (unpublished).
[12] J. E. Ortega and F. J. Himpsel, Appl. Phys. Lett. **64**, 121 (1994).
[13] J. Mathon *et al.*, Phys. Rev. Lett. **74**, 3696 (1995).
[14] This thickness dependence is not found during RT evaporation of the first layer, where the spectrum looks always similar to the bulk one (top curve of Fig. 3).
[15] P. M. Echenique and J. B. Pendry, J. Phys. C **11**, 2065 (1978).
[16] We have to note that the assignment of the different features in the top panel of Fig. 4 to a specific quantum number n can be varied, but other options lead to a much worse fitting in the structure plot and unrealistic oscillation periods, either too short (below 1.4 ML) or too long (above 8 ML).
[17] Another higher frequency (3.2 ML) would reproduce the same oscillation, but this value does not match the behavior observed in the structure plot.
[18] D.-J Huang *et al.*, Bull. Am. Phys. Soc. **40**, 412 (1995).