Spin Polarization of Quantum Well States in Copper Thin Films Deposited on a Co(001) Substrate

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Spin polarized photoemission is used to examine the spin polarization of the quantum well states observed in copper films grown on a fcc Co(001) substrate. The states are observed to predominantly carry minority spin polarization and this is shown through comparison with calculation to reflect a preferential hybridization in the interface. The calculation also provides evidence that the quantum well states observed in the experiments are not only *sp* derived but also reflect the hybridization with the more localized copper *d* bands.

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Oscillatory exchange coupling in magnetic multilayers is currently attracting considerable interest [1]. In a number of different systems, including Fe/Cr [2] and Co/Cu [3] multilayers, it has been shown that the coupling between adjacent ferromagnetic layers is strongly dependent on the thickness of the intervening spacer layer. Several different theoretical treatments have proposed that the coupling between the adjacent ferromagnetic layers may represent a modification to the RKKY theory previously developed to explain the coupling between magnetic impurity ions in different host materials [4,5]. In the magnetic multilayers, however, the experimentally observed periodicity is not consistent with a free electron Fermi surface, but rather that reflecting the discrete periodicity of the intervening layer [4]. These "aliasing" theories consider the intervening layer in terms of the bulk band structure and predict oscillation periods $2\pi/q$ where q, the nesting vector, is given by $2k_F - G$ with G the appropriate reciprocal lattice vector. However, the finite thickness of the intervening layer or any related thin film will lead to a quantization of the bulk band structure in the direction perpendicular to the film. Indeed, several studies of noble metal films deposited on ferromagnetic substrates have shown that discrete or quantum well states do exist [6–8] and, furthermore, that these states cross the Fermi level with a periodicity similar to that observed for the magnetic coupling in the multilayers [7,8]. Combined with the observation that in the Ag/Fe(001) system, the related interface states are highly spin polarized [6], it has been suggested that in the multilayers, the *sp*-like quantum well states in the intervening layer transmit the magnetic coupling between adjacent ferromagnetic layers [8]. This is not unreasonable because the states effectively define the Fermi surface which is invoked in the RKKY-like theories of the coupling [4].

In this Letter we explore this suggestion further by examining the spin polarization of the quantum well states that are observed when Cu is deposited on a fcc Co(001) substrate. The Co substrate differs from the Fe(001) substrate used in our earlier study in that it does not have a band gap spanning the Fermi level for either spin component [9]. It has been suggested elsewhere that spin dependent reflectivities in the vicinity of such band gaps lead to the trapping of a single spin component or the polarization of the quantum well states within the intervening nonmagnetic layer [8].

As in the earlier studies of the Cu/Co(001) system, we observe the quantum well states crossing the Fermi level with a periodicity similar to the observed long period oscillations for the related multilayer [10]. For all thicknesses that we are able to measure, we find that the quantum well states show minority spin polarization, even for the thicker copper films. Using a tight-binding scheme, we show that it is impossible to model these states and obtain the same spin polarization, which clearly reflects enhanced hybridization between the states and the minority spin states in the substrate. We further show that the presence of localized Cu *d* states strongly hybridized with the Cu *s-p* bands cannot be ignored.

All of the experiments described in this paper were carried out on the U5 spin polarized photoemission facility at the National Synchrotron Light Source (NSLS). Described in more detail elsewhere [11], the photoemitted electrons are energy and momentum analyzed with a commercially available hemispherical analyzer before passing into a low energy diffuse scattering spin detector of the type described by Unguris and co-workers [12]. The photons are provided by a UV undulator installed on the UV ring at the NSLS.

The Co crystal is prepared by depositing Co onto a freshly cleaned Co(001) substrate to a thickness of approximately 20 monolayers. Earlier structural studies have shown that Co(001) films grown in this manner are tetragonally distorted in the perpendicular direction [13]. Having grown the Co film, different thicknesses of copper overlayer are then deposited. Deposition rates are monitored by the use of Auger electron spectroscopy, quartz crystal monitors, and a quadrupole mass spectrometer. As a final monitor of the copper thickness, spin polarized photoemission spectra from a second Co film of thickness of the order of 6–7 monolayers deposited onto the different copper films were measured to confirm earlier measurements of the thickness dependent exchange cou-

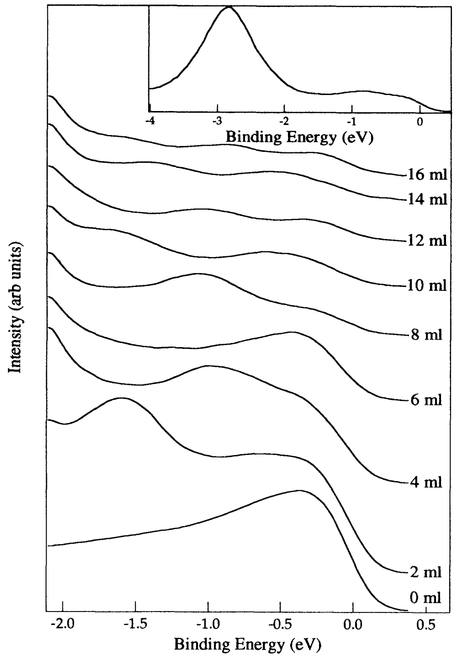

FIG. 1. Photoemission spectra recorded from different thickness copper films deposited on a Co(001) substrate as indicated. The binding energy is referenced with respect to the Fermi level. The incident photons are p polarized with an energy of 24 eV. The inset shows a spectrum recorded from a 4 monolayer thick copper over a wider energy range.

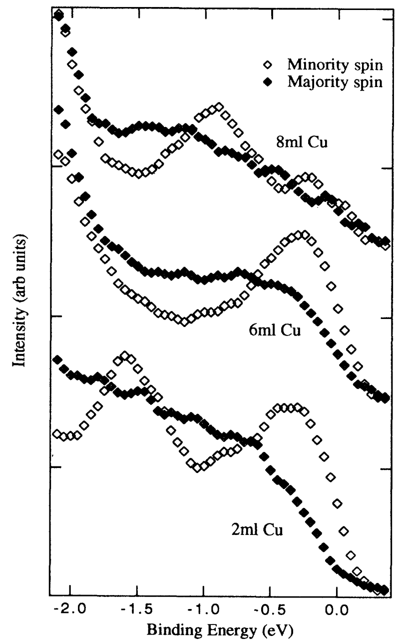

FIG. 2. Spin resolved photoemission spectra recorded from 2, 6, and 8 monolayer thick copper films. The incident photons are p polarized with an energy of 24 eV.

pling [10]. Note that the mean free path of the photoelectrons limits the polarization measurement in these latter experiments to the outer Co film. Surface order in the substrate and overlayer films is monitored with low energy electron diffraction.

Figure 1 shows the spin integrated photoemission spectra obtained from copper films as a function of the copper thickness. We estimate that the indicated number of monolayers is accurate to within 1 monolayer. The spectra are measured along the surface normal and the energy of the incident photons is 24 eV. The spectra clearly show that the quantum well states that evolve in the region from the Fermi level down to a binding energy of 2.0 eV. The inset shows the photoemission spectrum recorded from a 4 monolayer thick copper film over a slightly larger energy range. The peak associated with the copper d bands is observed in the region between 2.5 and 3.0 eV binding energy.

The binding energies observed for the quantum well states in this study compare favorably with the binding energies observed in the earlier studies [8]. Thus the spectra would suggest that the first Fermi level crossing for these states occurs at a copper thickness of the order of 5–6 monolayers. As noted earlier, confirmation of this thickness is obtained by depositing a second Co film of thickness 6–7 monolayers down on top of the Co film. Spin polarized photoemission studies of this second Co layer confirm that for 5–6 monolayers of Cu the coupling between the adjacent Co layers is antiferromagnetic. Repeating this experiment on a copper film with thickness equivalent to 8 monolayers shows that the coupling has reverted to ferromagnetic.

Figure 2 shows the results of our spin polarized photoemission study of these states at three different thicknesses. The spectra are again recorded with an incident photon energy of 24 eV and with electron emission along the surface normal. As in our earlier study of the Ag/Fe(001) system [6], the states all show minority spin polarization. The spectrum recorded from the 2 monolayer copper film shows the quantum well state with minority spin at a binding energy of 1.5 eV and a second minority spin feature close to the Fermi level. We associate the latter peak with emission from the substrate. The spectrum recorded from approximately 6 monolayers of copper clearly shows that as the state passes through the Fermi level it is still showing minority spin polarization even though it is now out of the even symmetry minority spin band gap associated with the substrate. The top of the latter band gap is at a binding energy of approximately 0.55 eV below the Fermi level. The spectrum from the 8 monolayer copper films shows that even for the thicker copper films the states show a strong spin polarization. The quantum well state in the latter spectrum crosses the Fermi level at a copper thickness of approximately 10–11 monolayers.

In order to obtain a better understanding of the photoemission spectra shown in Figs. 1 and 2 we have calculated the electronic structure of different thickness copper films on a fcc Co substrate using a spin dependent tight-binding scheme in a slab formulation. Described in more detail elsewhere [14], these tight-binding calculations are carried out using an effective Hamiltonian of the form

$$H=\sum_{\mathbf{k}} E(\mathbf{k})n_{\mathbf{k}}+(U/N)\sum_{\mathbf{k},\mathbf{k}'} n_{\mathbf{k}\uparrow}n_{\mathbf{k}'\downarrow}\,, \tag{1}$$

where the first term reflects the nonmagnetic band structure and the second term represents the modification due to an on-site spin-dependent potential U. The latter "exchange" potential is simply taken as the effective Stoner parameter calculated in several local spin density calculations of the susceptibility of the relevant elements [15]. It has been demonstrated elsewhere [16] that the latter parameter is essentially an atomic property showing little variation from one environment to another. Our approach then is to take the two-center parameters associated with a tight-binding fit to the nonmagnetic band structure [17], split the on-site spin-dependent energies for the d blocks by an amount Δ and, in the case of our nonorthogonal fit, make appropriate adjustments to the associated off-diagonal elements. The cobalt-copper interaction parameters were taken as the mean of the cobalt and copper parameters. Where required the scaling scheme of Anderson and Jepsen was used [18]. The on-site energies were adjusted to align the Fermi levels of the two metals. The lattice constants for both materials were set equal to 3.61 Å. The spin-dependent densities of states are integrated up to the Fermi level to obtain the resulting layer-dependent moments. A self-consistent solution is sought such that for each layer

$$\Delta_l=U_l m_l\,, \tag{2}$$

where Δ_l is the layer-dependent splitting introduced into the d block, U_l the layer-dependent Stoner parameter, and m_l the calculated moment for each layer. The total density of states was calculated for each overlayer system by summing over 28 k points evenly distributed throughout an irreducible triangle in the surface Brillouin zone. Charge neutrality for the system as a whole is maintained throughout the calculation.

In order to make a more direct comparison with the photoemission spectra recorded along the surface normal, we show in Fig. 3 the calculated spin-dependent density of states in a narrow region around $\bar{\Gamma}$, the Brillouin zone center as a function of copper thickness. The layer-dependent charge densities corresponding to the different eigenvalues are weighted by factors reflecting the relative photoionization cross sections for cobalt and copper [19] and the mean free path of the photoemitted electrons. For the present calculations the latter was set at 6.5 Å.

In both the calculated majority and minority spin "spectra" shown in Fig. 3 a peak is observed at a binding energy of 2.75 eV which corresponds to the main emission from the copper d bands. In the region between this peak and the Fermi level we observe a series of smaller peaks moving up to and through the Fermi level, well resolved in the minority spin channel but less obvious in the majority spin channel. The indicated peaks in the minority spin channel correspond to the minority spin quantum well states observed in the experiment with the first Fermi level crossing occurring in the vicinity of 5–6 monolayers. The strong minority spin peak at the Fermi level in the 2 monolayer film corresponds to the Co derived feature observed in the equivalent experimental spectrum in Fig. 2. Close examination of Fig. 2 shows that there is also structure in the background of the experimental majority spin spectra that may reflect the presence of peaks. However, the intensity is such that no real comparison can be made with the calculated spectra.

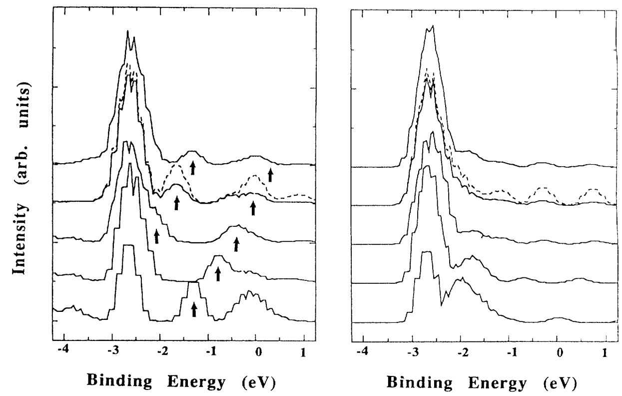

FIG. 3. Calculated spin resolved photoemission "spectra" from different thickness copper films. The left-hand panel shows minority spin spectra and the right-hand panel shows majority spin spectra. The copper thicknesses range from 2 through 6 monolayers from bottom to top in each panel. The dashed lines indicate spectra calculated for the 5 monolayer films with equal weight given to s, p, and d states. The arrows indicate the relevant quantum well states in the minority spin panel.

Examination of the eigenvectors or charge densities associated with our calculated quantum well states shows that they reflect hybridization of the copper s-p bands with the more localized copper d bands. It is the spin polarization carried in these d bands that results in the spin polarization of the quantum well states calculated in Fig. 3. Indeed, because of the use of atomic photoionization cross sections in our calculation, the calculated spectra shown in the figure are effectively a measure of the d band density of states, d-DOS, in the copper films and interface. As a comparison, we also show in the figure spectra calculated for the 5 monolayer copper films if we give equal weight or photoionization cross sections to the s, p, and d components. The spectra still show the minority spin states to be the dominant component, although now the majority spin states are better defined. Note that the difference between the dashed lines, equally weighted, *s*, *p*, and *d* components, and the solid lines, *d* component, provides us with a measure of the relative *d* weight in the quantum well states.

The spin polarization of the quantum well states reflects the preferential hybridization with the substrate minority spin *d* bands. Indeed all of the observed states show a large minority spin charge density of *d* character on the cobalt layer immediately at the interface. A simple perturbation expansion would suggest that hybridization at the interface has to favor minority spin because the mean binding energy of the minority spin *d* bands for the cobalt is much closer to the Fermi level than the equivalent for the majority spin. The presence of the substrate band gap which is also centered around the mean binding energy of the *d* bands leads to a strong localization of the Co component of these states in the outer layers of the Co.

In summary our spin polarized photoemission studies indicate the quantum well states observed in copper films grown on a Co(001) substrate are strongly polarized preferentially with minority spin character. The spin polarization reflects the hybridization at the interface between the two layers which clearly favors minority spin. Our calculation also indicates that the spin polarization is carried in both the *s-p* bands and the copper *d* bands with which these states are hybridized. We believe this represents the first demonstration of how the noble metal *d* bands may be involved in the magnetic coupling of the related multilayer systems. The presence of spin polarized bands crossing the Fermi level clearly indicates that the copper atoms will carry a small magnetic moment. However, in the present study we are unable to assign any value to that moment.

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[1] E.g., *Magnetic Surfaces, Thin Films, and Multilayers,* edited by S. S. P. Parkin, H. Hopster, J-P. Renard, T. Shinjo, and W. Zinn, MRS Symposia Proceedings No. 231 (Materials Research Society, Pittsburgh, 1992).

[2] M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, F. Pretroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988); J. Unguris, R. J. Celotta, and D. T. Pierce, Phys. Rev. Lett. **67**, 140 (1991).

[3] M. T. Johnson, S. T. Purcell, N. W. E. Mcgee, R. Coehoorn, J. ann de Stegge, and W. Hoving, Phys. Rev. Lett. **68**, 2688 (1992).

[4] P. Bruno and C. Chappert, Phys. Rev. Lett. **67**, 1602 (1991).

[5] Y. Wang, P. M. Levy, and J. L. Fry, Phys. Rev. Lett. **65**, 2732 (1990); R. Coehoorn, Phys. Rev. B **44**, 9331 (1991); D. M. Edwards, J. Mathon, R. B. Muniz, and M. S. Phan, Phys. Rev. Lett. **67**, 493 (1991); F. Herman, J. Sticht, and M. Van Schilfgaarde, in *Magnetic Surfaces, Thin Films, and Multilayers* (Ref. [1]), p. 195.

[6] N. B. Brookes, Y. Chang, and P. D. Johnson, Phys. Rev. Lett. **67**, 354 (1991).

[7] J. E. Ortega and F. J. Himpsel, Phys. Rev. Lett. **69**, 844 (1992).

[8] J. E. Ortega, F. J. Himpsel, G. E. Mankey, and R. F. Willis, Phys. Rev. B **47**, 1540 (1993).

[9] E.g., C. M. Schneider, J. J. de Miguel, P. Bressler, P. Schuster, R. Miranda, and J. Kirschner, J. Electron. Spectrosc. **51**, 263 (1990).

[10] Z. Q. Qiu, J. Pearson, and S. D. Bader, Phys. Rev. B **46**, 8659 (1992).

[11] P. D. Johnson, S. L. Hulbert, R. Klaffky, N. B. Brookes, A. Clarke, B. Sinkovic, N. V. Smith, R. Celotta, M. H. Kelly, D. T. Pierce, M. R. Scheinfein, B. J. Waclawski, and M. R. Howells, Rev. Sci. Instrum. **63**, 1902 (1992).

[12] J. Unguris, D. T. Pierce, and R. J. Celotta, Rev. Sci. Instrum. **57**, 1314 (1986); M. R. Scheinfein, D. T. Pierce, J. Unguris, J. J. McClelland, R. J. Cellota, and M. H. Kelley, Rev. Sci. Instrum. **60**, 1 (1989).

[13] A. Clarke, G. Jennings, R. F. Willis, P. J. Rous, and J. B. Pendry, Surf. Sci. **187**, 327 (1987).

[14] P. D. Johnson, Y. Chang, and N. B. Brookes, in Proceedings of X VUV Conference (World Scientific, Singapore, to be published).

[15] J. F. Janak, Phys. Rev. B **16**, 255 (1977).

[16] S. Ohnishi, C. L. Fu, and A. J. Freeman, J. Magn. Magn. Mater. **50**, 161 (1985).

[17] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[18] E.g., O. K. Andersen and O. Jepsen, Physica (Amsterdam) **91B**, 317 (1977).

[19] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).