Photoemission study of quantum confinement by a finite barrier: Cu/Co(wedge)/Cu(100)

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Quantum confinement is studied with angle-resolved photoemission for ultrathin Cu separated from the Cu(100) substrate by an epitaxial wedge of Co (0–11 Å) that serves as a finite barrier. For 2 ML of Cu, the photoemission intensities of the Cu *sp* quantum-well (QW) state at 1.6 eV binding energy and the corresponding *d*-band-derived QW state at 2.4 eV increase rapidly with the thickness of the Co barrier and indicate stronger confinement of the *d* QW state than of the *sp* state. Implications for the magnetic coupling and magnetoresistance are discussed.

I. INTRODUCTION

Quantum-well (QW) electronic states have been well studied in semiconductor heterostructures. Recently the QW concept has been extended to metallic systems, especially in relationship to giant magnetoresistive heterostructures. The utility of the concept in this latter context comes from the need to describe the electronic structure of metallic spacers in the ultrathin regime where the electrons experience not only the periodic bulk potential, but also the potential discontinuities at the surfaces and/or interfaces. QW states in metals have been studied with electron spectroscopies in many systems.[1–9] For noble metals on ferromagnetic substrates, the *sp*-band-derived QW states are spin polarized with mainly minority character[3,5] and give rise to the oscillatory interlayer magnetic coupling.[4,10,11] The change in magnetic coupling is accompanied by a giant, negative magnetoresistance (MR) for the Co/Cu multilayer system. While the existence of the *sp* QW states has been identified in metals, there is also interest in how the *confinement* of both *sp* and *d* QW states evolves with the height and width of the barriers, and their relationships with the magnetic properties.

We have performed a photoemission study on Cu QW states confined by a wedge-shaped Co layer grown epitaxially on a Cu(100) substrate. The quantization of Cu *d*-derived states was observed for the first few monolayers of Cu on Co. The confinement is demonstrated by scanning the changes in intensities of QW states associated with 2 ML of Cu deposited on the Co wedge. The degree of confinement for the *d* QW state is observed to be more pronounced than for the *sp* QW state.

The confinement helps us to understand from an electronic structure point of view the role of ultrathin barrier layers in influencing the MR. For example, Parkin[12] recently showed that the addition of a second ultrathin ferromagnetic layer at the interfaces of ferromagnetic-nonmagnetic-ferromagnetic sandwiches or multilayers can change the MR exponentially with increased thickness. The effect saturates with a characteristic length of only 1.5–3 Å. Since the giant MR is related to the electronic structure in the spacer material,[3–5] the question we will address is what governs the effect of the additional ultrathin magnetic layer.

II. EXPERIMENT

Angle-resolved photoemission experiments were performed at the U5 undulator beam line[13] at the National Synchrotron Light Source, Brookhaven National Laboratory. The Cu(100) single crystal was cleaned with sputtering and annealing (600 °C) cycles in an end station with base pressure of 1×10^{-10} Torr. Co and Cu were deposited at a typical rate of 0.5–1 Å/min with pressure rise $<5\times10^{-10}$ Torr. Face-centered-cubic Co and Cu are known to grow epitaxially in a layer-by-layer mode onto each other at room temperature.[14] Epitaxy was confirmed with low-energy electron diffraction, and is comparable with that of the samples in Ref. 14. The deposition rate was monitored with a quadrupole mass spectrometer and calibrated with the photoemission intensities of Cu and Co 3*p* core levels within an accuracy of ~20% for Co.[15] The Cu thickness is known with a better accuracy (±0.2 ML) due to further calibration with the appearance of the Cu *sp* QW states. Wedge-shaped Co layers were produced by moving the sample behind a fixed mask during deposition, similar to the procedure used in our magneto-optic studies.[14,17,18] The typical slope of wedge was 1–1.5 Å/mm. The spot size of the light on the sample was ~1 mm. The total energy resolution was 0.15–0.20 eV. All spectra were taken at normal emission with a photon energy of $h\nu=22.7$ eV, unless otherwise specified. The intensities of the spectra were normalized to the counts above the Fermi energy E_F, which arise form the secondary-electron emission of the higher-order light. The spectra for different Co thicknesses were taken by moving different parts of the Co wedge into position. The Cu thickness dependence of the spectra was obtained by sequential depositions before each measurement. The cleanliness of the substrate and films was confirmed by the absence of C and O valence-

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band photoemission features. No impurity features at ~6 eV or between 10 and 20 eV were observed.

III. RESULTS AND DISCUSSION

Figure 1 demonstrates the development of the QW states of Cu deposited on thick Co (40 Å) previously grown onto a Cu(100) substrate. Shown in the inset are the calculated Cu bulk bands[19] along ΓX (with an 8% self-energy correction), which agrees with experimental band mapping.[20] The spectra of thick Co and of the Cu(001) single crystal are also included in Fig. 1. The *sp*-band (Δ_1 in Fig. 1 inset) derived QW states at 0–2 eV below E_F shift in energy with the change of Cu thickness, as was well documented previously.[3–5] The existence and sharpness of these QW states in our data indicate that the films are of good quality (i.e., the surfaces are smooth and clean). In addition, the Cu *d*-band feature(s) at ~2–3 eV also evolve with the change in Cu thickness. Most notably, the *d*-electron feature splits into two peaks for 2 ML of Cu. For films thicker than 3 ML, it becomes difficult to distinguish individual peaks within the region of the *d* states. However, the width of the *d* features is broader than that of the bulk *d*-band direct transition (~2.8 eV in binding energy). The *d* spectral shape also changes with Cu thickness, which suggests the coexistence of several states. At 2 ML of Cu, none of the states shows energy dispersion for photon energies between 20 and 80 eV, indicating that they are two-dimensional states. While hybridization of Cu and Co states exists for this thickness range,[3] the *discrete* nature and the *nonmonatonic* shifts in energy of these states with thickness suggest that finite-size effects are still crucial for their formation. Therefore, we regard the Cu *d* states as QW states down to the monolayer limit, analogous to the *sp* states,[4] where they also can be viewed as interfacial states.[3]

The symmetry character of the states for 2 ML of Cu on fcc Co are identified in Fig. 2. The spectra were taken with either predominantly *s*-polarized ($\alpha = 35°$) or *p*-polarized ($\alpha = 67°$) light. At normal emission along the ΓX line the dipole selection rule indicates that *p*-polarized light excites the *sp* band with Δ_1 character, while *s*-polarized light excites the *d*-derived Δ_5 band. The Δ_2 and Δ_2' bands (see Fig. 1 inset) in the same energy range are not observable in photoemission. The feature at 1.6 eV is enhanced by *p*-polarized light, indicating that it originates from the Δ_1 band with *s*, p_z, and/or d_{z^2} character. The other two states at 2.4 and 3.0 eV are enhanced by *s*-polarized light, indicating that they are both derived from the Δ_5 band with mainly $d_{xz,yz}$ character. This identification confirms that the 2.4- and 3.0-eV features both originate from the same bulk band, i.e., the *d*-derived Δ_5 bands of Cu, and are split only because of finite-size effects. For convenience, we denote the 1.6-eV states as *sp* QW states and the 2.4- and 3.0-eV states as the *d* QW states. Since the emission at 3.0 eV includes bulk band features, we tend not to focus on it in the remainder of the paper.

The *d* QW states are analogous to the well-studied *sp* QW states in that the potential discontinuity at the surfaces and/or interfaces exist for both *sp*- and *d*-band electrons. While the *sp* QW states in noble metals have been observed by several groups,[2–5] it is only recently that the quantum confinement of *d* states has been reported.[8,9] In our data, the discrete features of the *d* band smear out after the first 3 ML. We expect similar behavior for *d* bands in other metals.

The spin-polarized photoemission spectra of the QW states for 2 ML of Cu are shown in Fig. 3. The *sp* QW

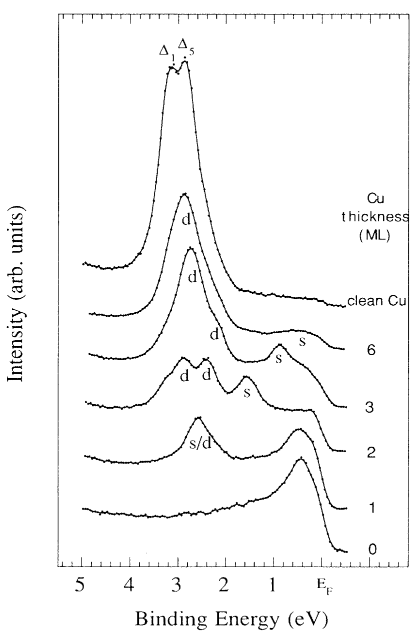

FIG. 1. Photoemission spectra ($h\nu = 22.7$ eV) of finite thickness Cu on 40 Å of fcc Co(001). Both the *sp* and *d* QW states are indicated. The spectra for clean Cu(001) and 40-Å Co(001) are also shown. Inset: calculated Cu bulk band structure along ΓX (Ref. 19).

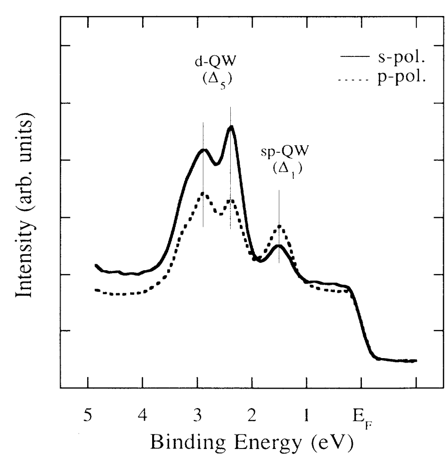

FIG. 2. Light polarization dependence of the photoemission spectra of 2 ML of Cu on ~20 Å of fcc Co(001), indicating that the states at 2.4 and 3.0 eV are Δ_5 derived (d) and the one at 1.6 eV is Δ_1 derived (sp).

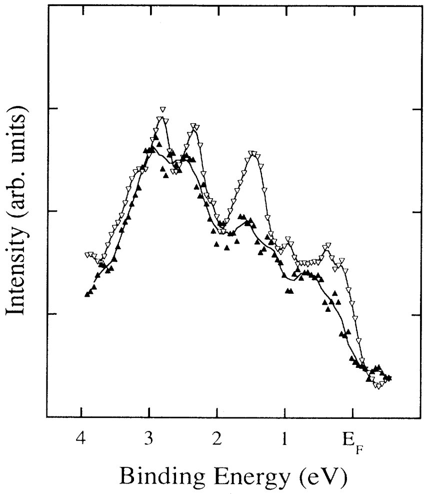

FIG. 3. Spin-polarized photoemission spectra of 2 ML of Cu on thick fcc Co(001). Solid triangle, majority spin; open triangle, minority spin.

state exhibits mainly minority character spin polarization, as observed in previous studies.[3,5] The *d* QW states also show minority spin character polarization, as observed in previous studies.[3,5] The *d* QW states also show minority spin character, which is not surprising given that the Co *d*-band barrier is spin polarized.

The dependence of the QW states on the thickness of the Co barrier is demonstrated in the sequence of spectra that appears in Fig. 4. A Co wedge of 0–11 Å (∼0–6 ML) separates the 2 ML of Cu from the Cu(100) substrate, as shown schematically in Fig. 4. It is apparent that the states at 1.6 eV (*sp* QW state) and 2.4 eV (*d* QW state) decrease in intensity with decreasing Co thickness, but show a negligible shift in energy within experimental error (±0.1 eV).

The integrated intensities of the QW states of interest were obtained by curve fitting the spectra, as shown in Fig. 5. The fitting procedure used is described as follows: the three discrete QW states (at 1.6, 2.4, and 3.0 eV) were characterized by broadened Lorentzians after first normalizing to the counts above E_F and subtracting both an integrated inelastic background and the experimentally determined Cu(100) spectrum (normalized to account for signal attenuation along the Co wedge). Figure 6 shows the evolution of the intensities of the 1.6- and 2.4-eV states as a function of the thickness of the Co barrier. It is clear that the intensities of both QW states increase with Co thickness. The *d* QW state (2.4 eV) saturates at ∼2 Å, while the *sp* QW state (1.6 eV) does not saturate until >6 Å.

We view the intensity changes with Co thickness as arising from partial quantum confinement of the electrons in the Cu by the finite Co barrier. The insert of Fig. 6 shows a diagram of the minority-band energy potentials felt by the electrons in the Δ_1 and Δ_5 bands. The diagram is constructed using the minimum of the measured bands for bulk fcc Cu and Co,[20] and the work function of single-crystal Cu. The Co layer is then represented as an energy barrier of finite height and width, which, with E_{vac}, defines the QW in the Cu overlayer. (The potential diagram for majority-spin electrons is similar, but with the Co barrier lowered by ∼1 eV.) The finite nature of the barrier allows the wave function of the QW states to partially leak out. This lowers the intensities of the states. As the width of the barrier approaches zero, the confinement vanishes, as do the QW states. The intensity changes of the QW states in Fig. 6 demonstrate the realization of a physical process in which the degree of

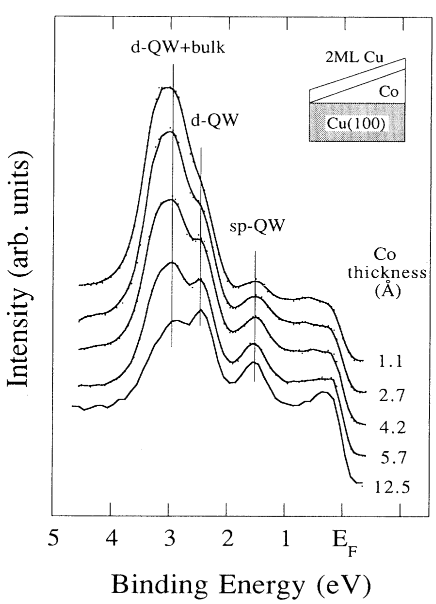

FIG. 4. Photoemission spectra of 2 ML of Cu separated from the Cu(001) substrate by a Co wedge. The structure is shown schematically.

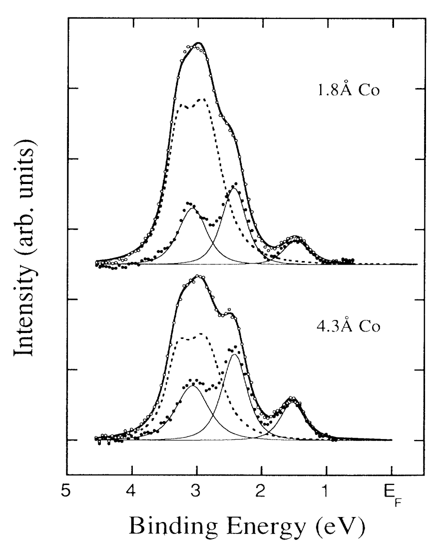

FIG. 5. Curve fitting for the spectra (after background subtraction) of 2 ML of Cu/Co (wedge)/Cu(100). Thick solid line, overall fitting result; dashed line, Cu substrate signal; thin solid line, QW states of the 2 ML of Cu.

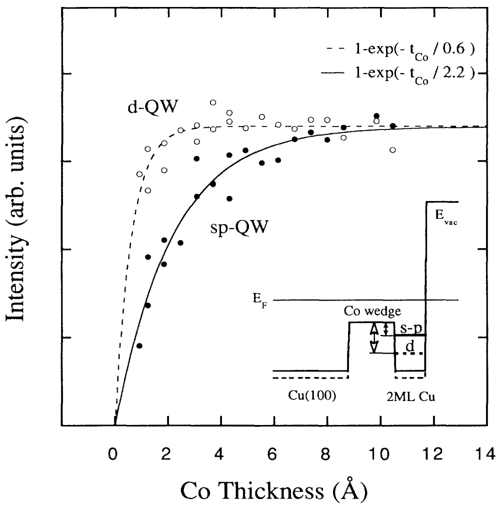

FIG. 6. Peak intensities of the *sp* QW state at 1.6 eV (solid circles) and *d* QW state at 2.4 eV (open circles; normalized to the same saturation intensity as the *sp* state) indicating a more pronounced quantum confinement by the Co barrier for the *d* QW state. Solid and dashed curves represent the experimental fits described in the text, where t_{Co} is the Co thickness. Inset: schematic of the minority energy potentials experienced by *sp* (thick solid line) and *d* (thick dashed line) electrons constructed based on the bulk band structures (Ref. 20). The energies for the two QW states of 2 ML of Cu (thin solid and dashed lines) and their energy differences from the top of the corresponding energy barriers (arrows) are also indicated.

confinement varies with the width of the energy barrier provided by the Co wedge. As a simple approximation, we fitted our data with exponentials, as shown in Fig. 6, with characteristic decay length of 2.2 ± 0.6 and 0.6 ± 0.2 Å for the *sp* and the *d* QW state, respectively. In principle, the energies of these states should also shift, due to the interference between the original wave and the reflected one, but such a shift is expected to be small.[21]

Figure 6 indicates that the *d* QW state is more strongly confined by the Co layer than the *sp* QW state. This can be understood qualitatively based on a one-dimensional square-well model in which the QW state wave functions decay exponentially into the Co barrier region with an imaginary wave vector κ, where

$$\kappa=\left[\frac{2m^*|V-E|}{\hbar^2}\right]^{1/2} . \tag{1}$$

The intensities of the partially confined QW states should scale with $(1-T)$, where the transmission T across the barrier is proportional to $\exp(-2\kappa a)$, where a is the barrier width. They therefore depend on $|V-E|$, the energy difference between the potentials in Co and the energy states in Cu, and the effective masses m^* of the electrons. The *d* QW state is bound in a deeper well than the *sp* state, as indicated by the arrows in the inset of Fig. 6. The *d* electrons also have a larger m^* perpendicular to the surface than the *sp* states, as shown in the bulk band structure (see the inset of Fig. 1).[19,20]. It is therefore not surprising that the wave function of the *d* QW state decays faster outside of the well and is more strongly confined than the *sp* QW state. The estimated κ values, using m^* f 1 and $3.6m_e$ and $|V-E|$ of 0.59 and 1.44,[20] are 0.39 and 1.16 Å^{-1} and the corresponding $(2\kappa)^{-1}$ decay lengths are 1.28 and 0.43 Å for the *sp* and *d* QW states, respectively.

A semiquantitative estimate of the decay lengths may be obtained from a tight-binding scheme that was used previously to examine QW properties.[3] Since the QW state couples to evanescent states that decay exponentially away from the interface, T can be shown to scale with the overlap, within the barrier, of the evanescent states coming from either interface, normalized to the barrier thickness. In the limit $\kappa a \gg 1$, both T and the overlap scale as $\exp(-2\kappa a)$. Using a tight-binding formalism to calculate the overlap of the evanescent states, we obtain characteristic decay lengths of 1.92 and 0.91 Å for the *sp* and *d* states, respectively. These calculated estimates are in better agreement with the experimental results of 2.2 and 0.6 Å than the estimates based on Eq. (1) above.

It is interesting to relate our confinement results to the MR experiments of Parkin[12] mentioned in Sec. I. The characteristic length for the *sp* QW states of 2.2 Å is similar to that of 1.5–3 Å reported by Parkin to describe the influence of an additional magnetic interfacial layer on the MR. Our implication is that the additional ultrathin interlayer provides a sufficient barrier to establish QW states in the spacer; the new QW states are determined by the barrier at the interface instead of by the primary ferromagnetic layer. Also, the similar characteristic length scales of 1.5–3 Å for different interlayer materials is not surprising given that the barriers heights provided by fcc Co, Ni, and Fe are not significantly different. Ortega *et al.*[22] proposed similar ideas on the relationship between the decay length within barriers and the interlayer magnetic coupling.

Ortega and Himpsel[4] demonstrated a correlation between *sp* QW states at E_F and the periodicity of the interlayer magnetic coupling. We now ask what role the *d* QW states play in this regard. We know that for nonmagnetic *transition-metal* spacers, both *sp* and *d* bands contribute to the Fermi surface. Bruno and Chappert,[23] Stiles,[24] and, more recently, Koelling[25] documented the multiple Fermi-surface spanning vectors that could give rise to a whole spectrum of coupling periods for transition-metal spacers. Experimentally, however, very few of these periods are found to survive. Koelling[25] suggested that for inhomogeneously strained interfaces, the spanning vectors that include significant *sp* character will be more robust, while the ones with predominantly of *d* character will tend to wash out (or dephase) due to interfacial roughness. Our observations are consistent with these ideas in that *d* QW states, even in transition metals, should exist only in the first monolayers and play no discernible role in the oscillatory magnetic coupling. Further, some spanning vectors associated with short-period oscillations have been shown to disappear below 8 ML due to hybridization that alters the Fermi surface.[26]

IV. CONCLUSION

We have demonstrated partial confinement of Cu quantum-well states by changing the width of a Co energy barrier that separates 2 ML of Cu from a Cu(100) substrate. The degree of confinement for the *sp* QW states is less than that for the corresponding *d* states. In addition, the successful use of a wedge technique in photoemission is promising for a broad range of electron spectroscopy experiments.

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$$\frac{I_{Co}}{I_{Cu}}=\frac{\sigma_{Co}}{\sigma_{Cu}}\frac{1-\exp(-t/\lambda)}{\exp(-t/\lambda)} .$$

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