Photoemission Study of Quantum Confinement by a Finite Barrier:
Cu/Co(wedge)/Cu(100)*

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The evolution of *d*-electron quantum-well (QW) states is observed with angle-resolved photoemission for ultrathin Cu epitaxially deposited on fcc Co(100). Quantum confinement is studied of the Cu *d*-QW state at 2.4 eV binding energy and the corresponding *sp*-state at 1.6 eV for 2ML of Cu separated from the Cu(100) substrate by an epitaxial wedge of Co (0-13ML) that serves as a finite barrier. The photoemission intensities indicate stronger confinement of the *d*-QW state than of the *sp*-state. Implications for the magnetic coupling are discussed.

73.20.Dx, 79.60.Bm, 75.70-i

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 surfaces/interfaces. QW states in metals, derived from *sp*-bands, have been studied with electron spectroscopies in alkali and alkali earth metals,¹ noble metals,^{2,3} Fe,³ Pb and Pb-In alloys⁴ and Hg.⁵ For noble metals on ferromagnetic substrates, the *sp*-band derived states are spin-polarized with mainly minority character,^{6,7} and give rise to the oscillatory interlayer magnetic coupling.^{3,8,9} The idea is that these electrons can be confined in a one-dimensional QW along the direction perpendicular to the film plane if they experience a sufficient potential barrier at the interfaces. Specifically, at the surface the energy barrier is formed by the vacuum level E_{vac} , and, at the metal-metal interface, by the corresponding (same symmetry character) band offset in the other metal. While the existence of the *sp*-QW states has been identified in metals, there is also interest in how the *confinement* evolves with the height and width of the barrier.¹⁰

We performed a photoemission study on Cu QW states confined by a wedge-shaped Co layer grown epitaxially on Cu(100). The quantization of Cu *d*-derived states was observed for the first monolayers of Cu on Co. The confinement is demonstrated by scanning the changes in intensities of QW states associated with 2ML of Cu deposited on the Co wedge. The degree of confinement for the *d*-QW state is observed to be larger than for the *sp*-QW state. Finally, possible relationships between *d*-QW states and magnetic coupling in multilayers are briefly considered.

Angle-resolved photoemission experiments were performed at the U5 undulator beamline 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 ultrahigh vacuum 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 $<5 \times 10^{-10}$ Torr. Fcc Co and Cu are known to grow epitaxially in a layer-by-layer mode onto each other at room temperature.¹¹ Epitaxy was confirmed with low-energy electron diffraction. 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 $\sim 20\%$ for Co. The Cu thickness has a better accuracy (± 0.2 ML) due to further calibration with the appearance of 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.¹¹⁻¹³ The typical slope of a wedge was 1-1.5 ML/mm. The spot size of the light on the sample was ~ 1 mm. The photoemission combined energy resolution was 0.15-0.20 eV. All spectra were taken at normal emission with photon energy of 22.7 eV. The intensities of the spectra were normalized to the counts above the Fermi energy E_F which arise from the secondary electron emission of the higher-order light. The spectra for different Co thicknesses were taken by moving the sample along the Co wedge. The Cu thickness dependence was obtained by sequential depositions after each measurement. The cleanliness of the substrate and films was confirmed by the absence of C and O valence-band photoemission features.

Figure 1 demonstrates the development of the QW states of Cu on thick Co (40 ML) grown onto the Cu(100) substrate. Shown in the inset are the calculated Cu bulk bands¹⁴ along ΓX (with 8% self-energy correction) which agrees with experimental band mappings.¹⁵ 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.^{3,6,7} 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 at 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 at this photon energy). The *d*-spectral shape also changes with thickness

suggesting the co-existence of several states. While hybridization of Cu and Co states exists for this thickness range,^{6,16} the *discrete* nature and the *non-monotonic* shifts in energy of these states with thickness suggest that finite size effects are crucial for their formation. (Hybridization with Co should merely shift the states in free standing Cu films slightly.¹⁶) We regard the Co *d*-states as QW states down to the monolayer limit³ where they also can be viewed as interfacial states.⁶

The symmetry character of the states for 2ML of Cu on fcc Co are identified in Fig. 2. The spectra were taken with either predominantly s-polarized ($\alpha=35^\circ$) or p-polarized ($\alpha=67^\circ$) 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 *d_{z²}* 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 both 2.4 and 3.0 eV features originate from the same bulk band, *i.e.*, the *d*-derived Δ_5 band 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.

The dependence of the QW states on the thickness of a Co barrier is demonstrated in the sequence of spectra that appears in Fig. 3. A Co wedge of 0-13ML separates the 2ML Cu from the Cu substrate, as shown schematically in Fig. 3. 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 negligible shift in energy within experimental error (± 0.1 eV). (The emission at 3.0 eV includes bulk band features, so we choose not to focus on it.)

The integrated intensities of the QW states of interest were obtained by curve fitting the spectra, as shown in Fig. 4. The fitting procedure used is described as follows: the three discrete QW states were characterized by broadened Lorentians after first subtracting both an integrated inelastic background and the experimentally determined Cu(100) spectrum (normalized to

account for signal attenuation along the Co wedge). Figure 5 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 ~1-2 ML while the *sp*-QW state (1.6 eV) does not saturate until >6 ML.

Our explanation for the intensity changes with Co thickness is the partial quantum confinement of the electrons in Cu by the finite Co barrier. The inset of Fig. 5 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 by taking the minimum of the measured bands for bulk fcc Cu¹⁵ and fcc Co¹⁷, and the work function of single-crystal Cu. The Co layer then is 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 barrier in Co lower by ~1eV.) The finite nature of the barrier allows the wavefunction of the QW states to partially leak out, which 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. 5 demonstrate the realization of a physical process in which the degree of confinement varies with the width of the energy barrier provided by the Co wedge. In principle, the energies of these states should also shift in the same process due to the interference between the original wave and the reflected one, but such a shift is expected to be small. The electronic coupling reported by McMahon *et al.*¹⁰ between two quantum wells of Ag separated by Cu or Au shows a similar intensity change and an energy shift only ~0.1 eV.

Figure 5 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 square-well model in which the QW state wavefunctions decay exponentially in the Co barrier with an imaginary wavevector κ , where

$$\kappa = \sqrt{\frac{2m^*|V-E|}{\hbar^2}} .$$

The intensities of the partially confined QW states depend on the differences $|V-E|$ between the energy states in Cu and the potentials in Co, and the effective masses m^* of the electrons. The d -QW state is bound in a well deeper than the sp -state, as indicated by the arrows in the inset of Fig. 5. 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).^{14,15} It is, therefore, not surprising that the wavefunction of the d -QW state decays faster outside of the well and is more strongly confined than the sp -QW state. As a first approximation, we fitted the data with simple exponential functions and estimate a κ value that is ~ 4 times larger for the d -QW state than for the sp -state.

The d -QW states are analogous to the well-studied sp -QW states in that the potential discontinuity at surfaces/interfaces exist for both sp - and d -band electrons. While the sp -QW states in noble metals have been observed by several groups,^{2,3,6,7} no report had been published previously on the quantum confinement of d -states [though data in Ref. 3 exhibit the relevant spectral features]. Even in our data, the discrete features of the d band smear out after the first 3 ML. The issue arises, then, as to why the d -QW states are hard to observe and disappear so rapidly when the films thicken. We suggest some possible answers: First, d -electrons intrinsically have shorter scattering lengths than sp -electrons and, therefore, lose phase coherence more abruptly. If the film is thicker than the scattering length of the electron, no QW state can form. Second, since the d -band disperses much less than the sp -band (~ 1.5 vs. ~ 5 eV, respectively), the energy differences for the d -states under different quantization conditions are smaller and more difficult to distinguish experimentally. Also, the existence of interfacial roughness could smear discrete states into a single broad feature. We are not sure which mechanism is mainly responsible, however, we expect similar behavior for d -bands in other metals where d -QW states smear out after the first several layers.

Another issue concerns the relationship of d -QW states to the properties of giant magnetoresistance multilayers. Ortega and Himpsel³ demonstrated the correlation between sp -

QW states at E_F and the periodicity of the interlayer magnetic coupling. For nonmagnetic *transition-metal* spacers, both *sp*- and *d*-bands contribute to their relatively complicated Fermi surfaces, and similar confinement effects are anticipated from both types of states. Bruno and Chappert,⁹ Stiles,¹⁸ and, more recently, Koelling,¹⁹ documented the multiple spanning vectors that could give rise to a whole spectrum of coupling periods for transition metal spacers. Experimentally very few of these periods survive. Koelling¹⁹ suggested that for inhomogeneously strained interfaces, the spanning vectors that include significant *sp*-character are most likely to be important in the coupling, while the ones with predominantly *d*-character would more readily be washed out (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.

In general, electron spectroscopy can probe where in *k*-space QW states emerge, and these regions presumably contain the bulk spanning vectors that govern the magnetic coupling periodicity. For example, Qiu *et al.*¹² experimentally observed a 3ML period for epitaxial Fe/Mo/Fe trilayers grown on Mo(100). Koelling¹⁹ suggested that the 2ML period due to nesting, analogous to that in Fe/Cr/Fe, is lost due to roughness of the lattice mismatched interfaces. For the 3ML period, Koelling identified two possible bulk spanning vectors in *k*-space along [100]: one contains significant *sp*-character and the other is predominantly of *d*-character. QW states therefore might be anticipated to emerge in the *sp*-admixed band but not in the other. This is a way that photoemission detection of QW states can directly enhance our understanding of oscillatory magnetic coupling in multilayers. Such explorations of transition metals will be fruitful to perform in the future.

In summary, we have observed *d*-band quantization in ultrathin Cu on fcc Co(001). Most interestingly, partial confinement of Cu quantum-well states is demonstrated by changing the width of a Co energy barrier that separates 2ML of Cu from a Cu(100) substrate. 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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FIGURES

- Fig. 1. Photoemission spectra ($h\nu=22.7$ eV) of finite thickness Cu on 40ML fcc Co(001). Both the *sp*- and *d*-QW states are indicated. The spectra for clean Cu(001) and 40ML Co(001) are also shown. Inset: calculated Cu bulk band structure along ΓX (Ref. 14).
- Fig. 2. Light polarization dependence of the photoemission spectra of 2ML Cu on ~ 20 ML 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. Photoemission spectra of 2ML Cu separated from the Cu(001) substrate by a Co wedge. The structure is shown schematically. The QW states at 1.6 and 2.4 eV decrease in intensity with decreasing Co thickness.
- Fig. 4. Curve fitting for the spectra (after background subtraction) of 2ML Cu / Co (wedge) / Cu(100). Thick solid line: overall fitting result; dashed line: Cu substrate signal; thin solid line: QW states of the 2ML Cu.
- Fig. 5. Peak intensities of the *sp*-QW state at 1.6 eV (solid circles) and *d*-QW state at 2.4 eV (open circles), indicating a stronger quantum confinement by the Co barrier for the latter. Inset: Schematic of the minority energy potentials experienced by *sp*- (thick solid line) and *d*- (thick dashed line) electrons constructed based on bulk band structures. The energies for the two QW states of 2ML Cu (thin solid and dashed lines) and their energy differences from the top of the corresponding energy barriers (arrows) are also indicated.

Fig. 2

Fig. 3

Fig. 4

Fig. 5