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Probing interfacial properties with Bloch electrons: Ag on Cu(111)

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The phase shift upon reflection of a valence Bloch electron in Ag at the Ag/Cu(111) interface is determined by angle-resolved photoemission. It shows a singularity at the band edge of Cu, allowing a determination of the substrate band-edge energy. The singular behavior is shown to be a characteristic interfacial property. A simple-model calculation reproduces the main features of the data.

One of the key issues involved in the electronic properties of the solid-solid interface is the determination and characterization of the interface potential. This subject of research has attracted considerable interest in recent years. The Schottky-barrier and band-offset problems for systems containing semiconductors are well-known examples.[1] Yet from a fundamental point of view, metal-metal interface systems are even more interesting. Due to the rather short screening length in metals, the bands do not bend as in semiconductors; therefore, metal-metal interfaces should provide a simpler environment for the examination of general interfacial properties. These systems also find important applications in superconducting and detector devices. This area of research, however, has been hindered by experimental difficulties. Most techniques for surface studies are not sensitive to an interface buried many atomic layers below the surface, and optical techniques (such as laser spectroscopies) are not suitable due to the opaqueness of metals.

The present study is an application of photoemission to deduce the interfacial properties. The system studied here is Ag(111) overlayers grown on Cu(111), a "model" system for which simple theoretical modeling can be easily performed. In this study, the Ag-Cu interface is probed by the valence Bloch electrons in the Ag overlayer in that an incident Bloch electron upon reflection from the interface undergoes a phase shift which is measured experimentally. The phase shift is an important parameter characterizing a scattering potential, and the relation between these is a subject of fundamental interest in quantum scattering problems.[2] The measured phase shift as a function of energy shows a singularity at the band edge of the Cu substrate. The singular behavior is shown to be a general interfacial property; thus, this method will allow an accurate determination of the band-edge energies for a substrate buried beneath an overlayer.

The phase shift is determined in photoemission by observing the interference (quantum-well) effects on the Bloch electron wave between the two boundaries of the Ag overlayer.[3,4] The density of occupied states, and hence the photoemission signal, exhibits peaks at energies satisfying the condition of constructive interference. Thus, even though the escape depth of the photoexcited electron is rather short,[5] an interface buried at a large depth below the surface can still be examined easily because the interference effect is inherently a ground-state property. In this sense, the interface is actually probed by the valence Bloch electrons in the Ag overlayer, which then convey the information through the photoemission process near the surface.

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin-Madison at Stoughton, Wisconsin. Several monochromators were used during many separate runs on both the 240-MeV ring Tantalus and the 1-GeV ring Aladdin. The photoemitted electrons were analyzed with a hemispherical analyzer having a full acceptance angle of 3°. The Cu(111) substrate was prepared by cycles of Ar ion sputtering and annealing. The Ag overlayers were prepared by evaporation from a tungsten crucible heated by a feedback-controlled electron beam. The overlayers were annealed at 200 °C briefly to enhance the film uniformity. The growth of Ag on Cu(111) under these conditions has been studied before.[6] The orientation of the Ag film is (111). The quality of the film is excellent as suggested by an exponential decay of the substrate photoemission signal as a function of overlayer thickness, the sharpness of the electron-diffraction pattern, and the existence of a sharp Ag(111)-like surface state observed in photoemission. An independent experiment was performed to calibrate the absolute overlayer thickness to within 10% accuracy.[7]

Several hundred photoemission spectra were taken for various overlayer thicknesses, photon energies, and emission angles. Figure 1 shows a typical subset of data for Ag overlayers of selected thicknesses taken with a normal-emission geometry. The large peak just below the Fermi level E_F is a surface state.[6] On the higher-binding-energy side, there are a number of quasiperiodic peaks whose energy positions evolve as a function of overlayer thickness. These peaks are the quantum-well states or resonances derived from the Ag *sp* valence band, as reported before in similar systems.[3,4] However, the present system exhibits intense quantum-well peaks over a wide energy range, in sharp contrast to Ag/Au(111) and Cs/Cu(111) systems studied previously which show in-

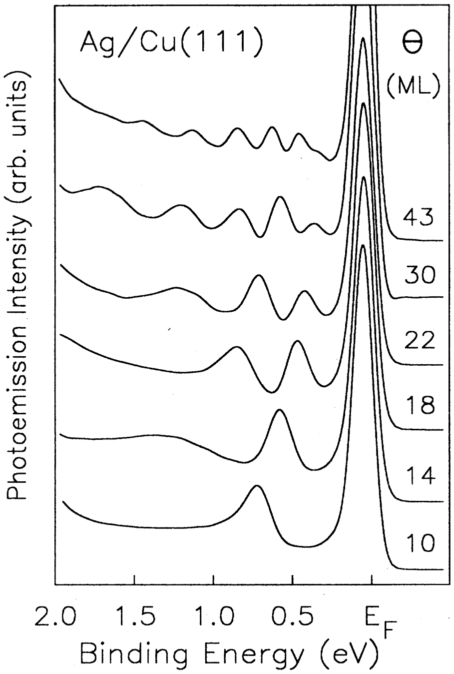

FIG. 1. Normal-emission spectra taken with a photon energy $h\nu = 10$ eV for Cu(111) covered with various amounts of Ag. The coverage Θ is expressed in terms of Ag(111) monolayers (ML). The binding-energy scale is referred to the Fermi level E_F.

tense peaks only above the substrate band edge.[3,4] The quantum-well peak positions are determined by the usual phase quantization rule (condition of constructive interference):

$$2k(E)d+\delta(E)=2n\pi\,, \tag{1}$$

where d is the quantum-well thickness, k is the Bloch wave vector, E is the electron energy, δ is the sum of the phase shifts at the Ag-Cu interface and the Ag-vacuum interface, and n is an integer (quantum number). In this equation, we have implicitly assumed that nonlocal effects are negligible for our rather thick overlayers, and therefore k and δ depend only on the energy and not on d. In the following analysis, d is taken to be the nominal overlayer thickness; a possible small correction on the order of an interatomic layer spacing, due to the finite extent of the surface and interface boundaries, has been ignored.

Figure 2 summarizes the energy positions of the peaks as a function of d for one typical set of data. The curves show the interpolated $E(d)$ functions for different n values; this interpolation allows us to treat d as a continuous variable. For a given E, and hence given k and δ, within the region of interest in Fig. 2, there typically exist several states with successive n values corresponding to different values of d. Equation (1) applies for each state; thus, several simultaneous equations can be set up with the same k and δ as unknowns. Solving this set of equations yields k and δ in terms of E. Since there are typically more equations than the unknowns (k and δ), the degree of consistency of the equations provides an independent check of the accuracy of the model. It turns out that the consistency is generally good, with some random data scattering that we attribute to experimental uncertainty. The good consistency implies that Eq. (1) is fairly accurate and that nonlocal effects are indeed negligible. The results for $k(E)$ [or, rather, $E(k)$] are shown in Fig. 3, where the origin of the horizontal axis is chosen to be the L point at the Brillouin boundary. Since d and k in Eq. (1) appear as a product, the 10% uncertainty in our absolute calibration of d will result in a corresponding scaling error in k in Fig. 3, but δ is not affected by this systematic error.[8] The solid curve in Fig. 3 is a least-squares fit to the data based on the usual two-band model, but with the free-electron mass m replaced by an effective mass m^* to account for multiband effects to the lowest order.[9] The fitting function is

$$\varepsilon(k)=E+2\varepsilon(p)-U-\{[2\varepsilon(p)-U]^2+4\varepsilon(p)E\}^{1/2}\,, \tag{2}$$

where E is referred to the band edge, $\varepsilon(x)\equiv\hbar^2x^2/2m^*$, $p\equiv\sqrt{3}\pi/a$ (a is the lattice constant), and $U=2.1$ eV is one half of the sp gap energy.[10] The fit gives $m^*/m=0.74$.

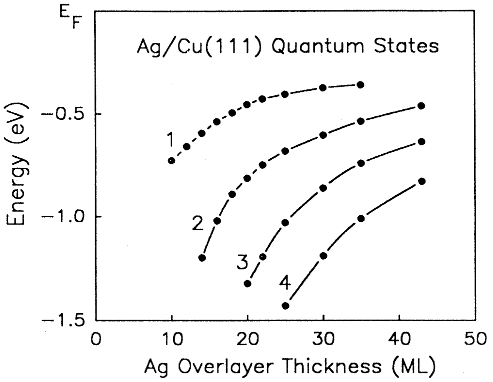

FIG. 2. The energy positions of the first four quantum-well states or resonances below E_F as a function of the Ag overlayer thickness (dots). The curves represent the interpolation of the data.

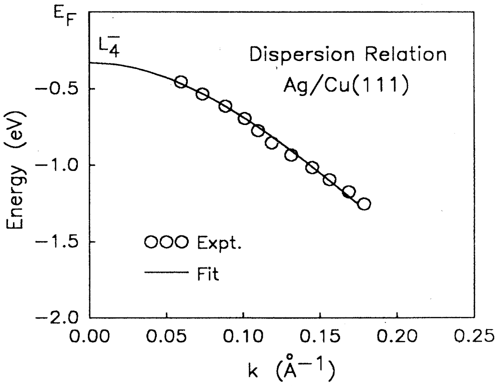

FIG. 3. The sp-band dispersion relation $E(k)$ for Ag along the [111] direction. The origin of the abscissa corresponds to the L point in the Brillouin zone. The circles are data points and the solid curve is a least-squares fit.

This band-dispersion relation is used below for the computation of δ.

The results for δ are shown in Fig. 4. The data points represent average experimental values, and the error bars indicate the observed data scattering. The data show a peak or singularity at $E = -0.85$ eV which corresponds to the known position of the *sp* band edge of Cu, the L_4^- critical point (the *sp* band dispersion of Cu is qualitatively similar to that shown in Fig. 3 for Ag).[11] It is easy to show that the singularity in δ is a general interfacial property resulting from the band edge in the substrate. Limited by space, however, the derivation will only be briefly outlined here just to indicate the essential points. The complex reflectivity $re^{i\delta}$ of a Bloch electron at the interface is an analytic function of the complex wave vector in the substrate by analytic continuation. Using the Cauchy-Riemann conditions, $\ln(r)$ and δ can be shown to satisfy the Laplace equation. For energies above the band edge of the substrate, $r = 1$ because energy conservation forbids the transmission of electrons through the interface. At the band edge, $dE/dk = 0$. Combining these results and with a little algebra, it is straightforward to show that a band edge in the substrate similar to the one shown in Fig. 3 leads to a singularity of the form

$$\delta_{\text{Ag-Cu}} \propto -(E-E_0)^{1/2}\Theta(E-E_0) , \tag{3}$$

where Θ is the unit step function and E_0 is the substrate band-edge energy. This singularity rides on top of a smooth function (including the contribution from the vacuum boundary). This equation has the same functional form as the familiar saddle-point-type van Hove singularity.[12]

The solid curve in Fig. 4 is the result of a calculation based on the two-band model, to illustrate the essential physics. The two interfaces are modeled as follows. The Ag (Cu) crystal potential is assumed to extend one half of an atomic plane spacing beyond the last atomic layer. Both interfaces are assumed to be abrupt. This is not a bad approximation for the Ag-vacuum interface since the energy range of interest is far below the vacuum level.[9] It is not bad either for the Ag-Cu interface as the metallic screening length is very short. The wave functions in Cu, Ag, and the vacuum are evaluated analytically and matched at the interfaces to obtain δ. The resulting somewhat lengthy analytic expressions, not shown here, contain band parameters as defined in Eq. (1) for both Cu and Ag and the work function (4.49 eV) of Ag(111).[13,14] This simple first-order model reproduces the essential features of the experimental line shape in Fig. 4; even the overall magnitude of the phase shift is about right.

The numerical discrepancy between the theoretical and experimental δ in Fig. 4 has two major contributions: the approximations involved in the modeling of the interface (abrupt interface) and the wave function (two-band model). An accurate modeling of the interface is beyond the capability of our experimental research program, and this study should stimulate theoretical efforts in this area. The two-band model, even though enhanced by the mass adjustment to account for multiband effects in an average manner, is expected to fail when the energy gets close to the Cu *d* bands which lie between 2–6 eV below the Fermi level. This effect probably accounts for the larger discrepancy on the higher-binding-energy side in Fig. 4.

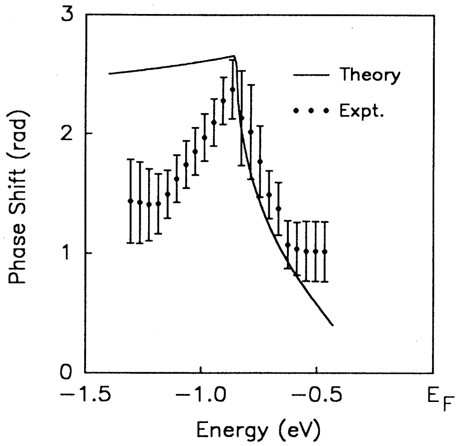

FIG. 4. The experimental phase shift (dots) and theory (curve) as a function of energy.

To summarize, well-defined quantum-well states and resonances are observed over a fairly wide binding energy range for Ag/Cu(111), a system with a large lattice mismatch. The results demonstrate that the interfacial properties can be studied by measuring the reflection phase shift of a Bloch electron. The phase shift is measured through an interference (quantum-well) effect on the density of states as probed by photoemission. It is shown that the phase shift exhibits singularities at band edges of the substrate; in addition to being of fundamental interest, this effect lends an important application in the determination of band-edge energies (of a substrate buried beneath an overlayer). The overlayers studied here are as thick as 43 atomic layers (~100 Å), defying the usual criticism that photoemission cannot probe a "real" interface. Numerous exciting possibilities exist for future experiments in which such measurements are refined and extended to other systems. For instance, it should be possible to deduce the band offset as well as the details of the interface potential for semiconductor-semiconductor interfaces.

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[7] Based on a variation of the method reported in Ref. 6.

[8] Our measured $E(k)$ agrees with the "best estimate" given by J. G. Nelson *et al.* [Phys. Rev. B **32**, 3465 (1985)], but differs in curvature from that obtained by R. C. Jaklevic and J. Lambe [Phys. Rev. B **12**, 4146 (1975)] using a thin-film tunneling technique. The discrepancy is most likely a result of errors in the absolute film thickness. Jaklevic and Lambe did not specify their accuracy; since our accuracy is 10%; it appears that they underestimated their film thickness by about 35 ± 10%.

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