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Minimum overlayer thickness for interface formation: An experimental study of the Cu/Ag/Cu(111) system

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The evolution of the electronic properties of the boundary between a solid (Ag) and an overlayer (Cu) as a function of the overlayer thickness is examined to yield the characteristic overlayer thickness for interface formation. The boundary properties are probed by measuring the reflection phase shifts of valence electrons using a quantum-well geometry.

Interfaces are crucial components in device architectures, and have attracted much interest in recent research activities. Many surface-sensitive spectroscopic techniques, such as photoemission, have been utilized for such studies.[1] Yet there exists a fundamental difficulty with many of these techniques, namely, the very short probing depth, and therefore these studies are usually limited to very thin overlayers deposited on a substrate. Under such circumstances, it is important to investigate the characteristic overlayer thickness at which the boundary properties approach those of a true interface (boundary between two semi-infinite solids). As the dimensions of modern device structures become smaller, it is also important to investigate the effects of boundary-boundary interactions.

A fundamentally relevant property at an overlayer-substrate boundary is the electronic potential. This is also the most important parameter for characterizing device performance, since it governs the flow of charges through the interface. An electron impinging upon a boundary may (partially) reflect and undergo a phase shift. A measurement of either the phase shift or the reflection coefficient (related by the Kramers-Kronig relations)[2] as a function of energy provides a complete specification of the boundary potential. The experiment to be reported here is a photoemission measurement of the phase shift of valence electrons in a Ag(111) substrate upon reflection from a Cu overlayer. From a determination of the asymptotic behavior of the phase shift at large Cu overlayer thicknesses, a characteristic overlayer thickness for interface formation is thus deduced. In our experiment, the Ag(111) substrate is itself a film with a finite thickness which is chosen to be large enough for its two boundaries to be decoupled, yet small enough for the film to exhibit a set of resolvable quantum states.[3,4] The motivation for this choice of geometry can be illustrated in terms of an acoustic analogy described in elementary physics textbooks: an organ pipe exhibits a set of acoustic resonances with frequencies depending on the ends of the pipe. If one of the ends is modified from being open to being closed, for example, the resonance frequencies will shift. These shifts are related to changes in reflection phase shift of the acoustic waves at the pipe end as a result of the modification in boundary conditions. Within this analogy, the Ag(111) film corresponds to the organ pipe, and the change in boundary conditions on one side is accomplished by changing the Cu overlayer thickness.

The photoemission experiment was conducted at the Synchrotron Radiation Center of the University of Wisconsin-Madison (Stoughton, Wisconsin). A normal-emission geometry was employed with a hemispherical photoelectron analyzer possessing a 3° full acceptance angle. The starting system was a Ag film prepared on a Cu(111) substrate. This system has been investigated previously, and is known to exhibit a highly ordered (111) film structure with an abrupt, lattice-mismatched interface (the solid solubilities of Cu in Ag and Ag in Cu are extremely small).[5] In the following, a monolayer (ML) of Cu or Ag is referred to a (111) monolayer in bulk Cu or Ag, respectively. The thicknesses quoted may have a systematic error less than 10% and random errors of about 5%.

The bottom curve in Fig. 1 is a normal-emission spectrum for an 18-ML Ag film on a Cu(111) substrate taken with a photon energy $h\nu = 10$ eV. The large peak just below the Fermi level is emission from a Ag(111) surface state. Two additional peaks at higher binding energies are emission from the discrete Ag valence states, known as the "quantum-well states."[3-5] As increasingly thicker Cu overlayers are deposited on the Ag film, the Ag(111) surface state evolves into a Cu(111) surface state at a higher binding energy.[6] Simultaneously, the quantum-well peaks shift toward lower binding energies as seen in Fig. 1. These energy shifts of the quantum-well states, due to the change in boundary condition, are generally much smaller than if simply more Ag (rather than Cu) were grown on top of the Ag film.[5] For example, the first quantum-well peak in Fig. 1 moves by about 0.02 eV with the deposition of 4 ML of Cu on the 18-ML Ag film, while previous results indicated an energy shift of about 0.05 eV if 4 ML of Ag were added on top of an 18-ML Ag film. The intensities of the Ag quantum-well peaks become diminished for increasing Cu overlayer thicknesses due to attenuation of the photoemission

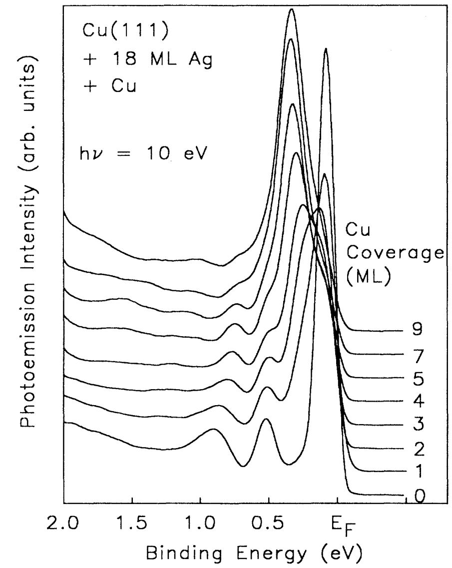

FIG. 1. Normal-emission photoelectron spectra taken with a photon energy $h\nu = 10$ eV for a Cu(111) substrate covered with 18 ML of Ag and further covered with various thicknesses of Cu as indicated. The binding-energy scale is referred to the Fermi level E_F.

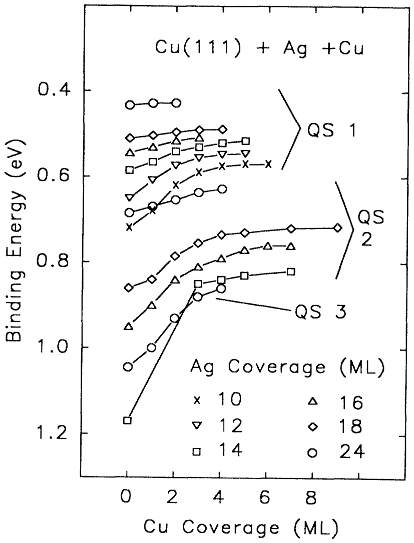

FIG. 2. The binding energies for the first three quantum-well states (QS1–QS3) in Ag films with thicknesses of 10, 12, 14, 16, 18, and 24 ML as functions of the Cu overlayer thickness. Data points for different Ag-film thicknesses are represented by different symbols as indicated; these are connected by line segments for clarity.

current by the overlayer. Again, this rapid attenuation is not observed if simply more Ag is grown on top of the Ag film.[5] This attenuation and the partial overlap with the surface-state peak (see the first quantum-well peak in Fig. 1) limit the range of measurement of the quantum-well peaks. A large number of samples were prepared and studied, including Ag films with thicknesses of 10, 12, 14, 16, 18, and 24 ML and Cu overlayer thicknesses in the range of 0–9 ML. The observed energy evolution of the Ag quantum-well peaks as a function of the Cu overlayer thickness is summarized in Fig. 2. For larger Cu overlayer thicknesses, the energies of the quantum-well states appear to be reaching well-separated asymptotic values, and the evolution is approximately exponential with a $1/e$ length scale on the order of 4 ML. For comparison, the energies of the quantum-well states for a growing Ag film on Cu(111) all converge to the top of the *sp* valence band with a characteristic inverse film-thickness dependence that was the basis for a previous band-structure determination.[5]

The quantum-well states within the Ag film satisfy the quantization rule

$$2k(E)d + \delta_0(E) + \delta(E,s) = 2n\pi \ , \tag{1}$$

where k is the wave vector, E the energy, d the Ag film thickness, δ_0 the phase shift at the Cu-substrate–Ag-film boundary, $\delta(E,s)$ the phase shift at the Ag-film–Cu-overlayer boundary, s the thickness of the Cu overlayer, and n an integer (quantum number).[3–5] Note that for $s \to \infty$, the system becomes a Ag quantum well sandwiched between two semi-infinite Cu crystals, and $\delta(E,s) \to \delta_0(E)$. For $s=0$, the system is a Ag overlayer on a Cu substrate, and $\delta(E,0) \equiv \delta_1(E)$ is simply the phase shift at the Ag-vacuum boundary. Varying the Cu overlayer thickness s leads to changes in δ, causing the quantum-well-state energies to shift. It can be shown based on simple algebra that the phase-shift evolution as a function of s should be similar to that seen in Fig. 2.

From the measured peak energies in Fig. 2 and the known dispersion relation $E(k)$ of the Ag valence band,[5] it is straightforward to deduce the total phase shifts $\delta_0(E) + \delta(E,s)$ at the two boundaries using Eq. (1). The results are shown in Fig. 3 by the circles. Since the data in Fig. 2 suggest an exponential behavior, we have chosen the following model function to describe the s dependence of the total phase shift:

$$\delta_0(E) + \delta(E,s) = 2\delta_0(E) + [\delta_1(E) - \delta_0(E)]\exp[-s/\lambda(E)] \ , \tag{2}$$

where λ is an energy-dependent "decay-length" parameter characterizing the range of influence of an interface. It is easy to verify that Eq. (2) correctly yields the limiting values at $s=0$ and ∞. Equation (2) is used to fit all of the data shown in Fig. 3, and the results are indicated by the various curves. In the fit, $\delta_1(E)$ is modeled by a quadratic polynomial, since it is expected to be a smooth, slowly varying function of E.[7] $\delta_0(E)$ is modeled by a quadratic polynomial plus a singularity term proportional to $-\theta(E-E_L)(E-E_L)^{1/2}$, where $E_L = -0.85$ eV is the band-edge energy of Cu and θ in the unit step function. This singularity term is a general result of the band edge discontinuity (just like the van Hove singularities in the density of states).[8] The function $\lambda(E)$ is also modeled by a quadratic polynomial. Overall, the fits in Fig. 3 are very good, and the small discrepancies can be accounted

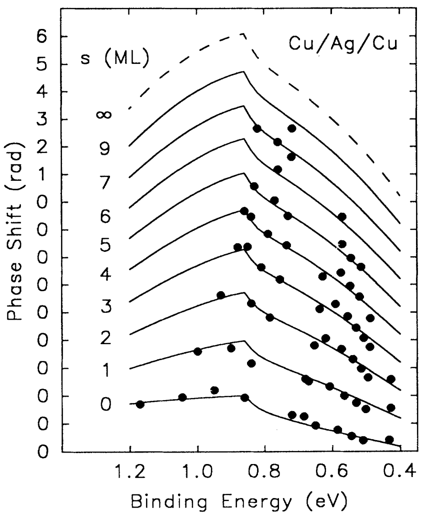

FIG. 3. The circles represent the experimental total phase shifts at the two boundaries of the Ag film as a function of the binding energy. Solid curves are fits to the data, and the dashed curve for *s*(Cu overlayer thickness)$\to\infty$ is a prediction based on the fit. Adjacent curves and data points for different *s* values are offset by 1 in the vertical direction for clarity.

for by errors in peak position assignment and layer thickness determination. Also included in Fig. 3 is a dashed curve showing the result of the fit for $s\to\infty$.

The result for $\lambda(E)$ from the fit is shown in Fig. 4, which is consistent with the estimate mentioned earlier that the decay length will be on the order of 4 ML based on a visual inspection of Fig. 2. The error bars shown indicate the approximate range of variation if higher-order polynomials are used in the fit. For instance, an assumed higher-order polynomial of $\lambda(E)$ yields a fit that is only slightly better than the one indicated. Various other fits were also performed by assuming higher orders of the polynomials for the phase shifts (with a corresponding increase in the number of fitting parameters). The fits were again only slightly better. In all of these other fits involving higher-order polynomials, the results clearly indicated a condition of over parameterization.[9] These results also indicate that the details in the assumed analytic form of the phase shift are not critical, and the most important feature of the data in Fig. 3 is the curve-to-curve variation. For example, the phase shift at 0.85-eV binding energy varies from about 2 rad at $s=0$ to about 4.7 rad at $s=4$ ML (where a data point exists) and at about 6 rad for the limit of $s\to\infty$. It is this variation that determines λ; the assumed analytic form of the phase shift is just a convenient way to interpolate the discrete set of data points.

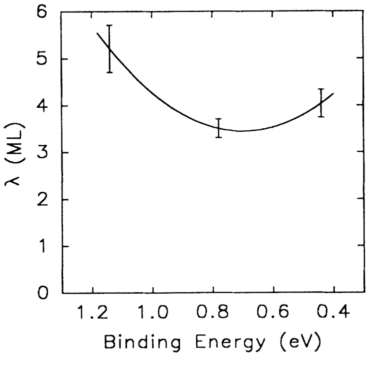

FIG. 4. The characteristic interface length λ [in terms of Cu(111) monolayers] as a function of the binding energy.

The decay length λ is the characteristic length for interface formation or the characteristic length for decoupling between the two boundaries of a thin film. Its values (~ 8 Å) determined here are much larger than the metallic screening length $l\approx 0.5$ Å as discussed in standard textbooks on solid-state physics.[10] The screening length is defined as the length scale for screening out an external potential. For example, the surface potential of a Cu single crystal could penetrate into the bulk only for a distance on the order of l. Thus, the interesting question here is why λ is much larger than l. The answer to that is that the estimate of the screening length as usually derived in textbooks is valid only for an infinite system. A thin film generally exhibits discrete states rather than a continuum as in the bulk, and its dielectric response will therefore be different (and less efficient in screening).

Ag films grown on Cu(111) show sharp quantum-well states, as see in Fig. 1. A similar experiment performed on the complementary system, Cu films grown on Ag(111), shows no evidence for such sharp states (data not shown due to space limitations). This is related to the band structures of these two materials; namely, the quantum well for a Cu overlayer on Ag(111) is an "antiwell" which cannot cause electron confinement.[4] The smooth (exponential) behavior seen in Fig. 2 is related to the lack of sharp quantum-well states in the Cu overlayers and the energy mismatch between the Ag and Cu valence bands; otherwise, an additional oscillatory behavior may be expected due to double-layer resonance and interference effects such as "resonant tunneling," which is known to be important in certain semiconductor device structures.[11,12] The discrete quantum states in an isolated Cu layer, if broadened by interactions with a substrate, will resemble the energy distribution of states in bulk Cu if the Cu layer thickness is sufficiently large. Presumably, this happens for Cu overlayers on Ag(111) at an overlayer thickness on the order of 4 ML, corresponding to the observed λ.

In summary, this work is a quantitative investigation of the evolution to interface formation as the thickness of an overlayer is increased. The method is based on an application of "quantum-well spectroscopy,"[3–5,8] in which a quantum-well geometry allows the probing of the boundary properties at various energies. The issue addressed here concerning the characteristic interface length is central to thin-film and multilayer research. An overlayer needs to be at least as thick as $(2-4)\lambda$ for the overlayer-substrate boundary to be properly called an interface. This criterion must be considered when interface studies are performed on very thin films using surface-sensitive techniques. λ is also a basic length scale for distinguishing superlattices from multiple-quantum-well systems.

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