# Overlayer Test of Surface Photoemission Effect in Cu(100)

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Angle-resolved photoemission from bulk valence bands of a single crystal yields direct-transition peaks that are often distorted due to interference with broadband indirect emission induced by the surface. The present study is a direct test of this surface effect by using an overlayer to modify the surface boundary condition. A Cu(100) single crystal exhibited a rather asymmetric *sp* direct-transition peak and a significant indirect emission intensity. Deposition of a thin Ag overlayer shielded the Cu surface from vacuum, and both the peak asymmetry and the indirect emission intensity were suppressed. [S0031-9007(97)02893-7]

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Angle-resolved photoemission from bulk valence bands of a single crystal yields well defined peaks corresponding to momentum conserving band-to-band optical transitions. These so-called direct-transition peaks disperse as a function of photon energy and emission direction, and a major application of angle-resolved photoemission has been to map the band structure based on a measurement of these peak dispersions [1]. It has been clear from old data published in the literature that the line shapes of these peaks are often asymmetric. This asymmetry was explained recently in terms of an interference effect between the direct-transition channel and a surface-induced indirect-transition channel [2]. For the latter, the relevant surface effect has a fairly short range, and therefore the indirect transition is momentum nonconserving and leads to a broadband emission from the valence band. This indirect emission remains phase coherent with the direct transition, and the interference between the two channels is very similar to the Fano effect in atomic physics. The dominant mechanism for indirect emission at low photon energies has been attributed to a nonvanishing $\nabla \cdot \mathbf{A}$ near the surface caused by a dielectric mismatch between the substrate and vacuum ($\mathbf{A}$ is the vector potential of the photon field, which changes rapidly across the surface). This $\nabla \cdot \mathbf{A}$ term should be part of the transition matrix element, but has been largely ignored in previous photoemission calculations.

Although the asymmetric line shape has been well explained, there has been no direct proof that it is actually caused by the surface. The present study is to address this issue. To prove the surface origin of the asymmetric line shape, we use an overlayer to modify the surface boundary condition. In particular, we use an overlayer material that provides an approximate dielectric match to the substrate to suppress the effect of the $\nabla \cdot \mathbf{A}$ term. This should suppress the indirect emission intensity as well as the asymmetry of the direct-transition peak. Both effects were indeed observed as we will report below. In our experiment, we used a single-crystal Cu(100), which exhibited a rather asymmetric direct-transition peak from the *sp* band. For the overlayer material, we chose Ag. This choice was based on several considerations. Ag, being an element in the same column of the period table, has very similar electronic properties, and thus provides a fairly good dielectric match resulting in a much reduced $\nabla \cdot \mathbf{A}$ at the interface. More importantly, Ag does not intermix with Cu, and grows in the (111) direction when it is deposited on Cu(100) [3]. This orientational difference results in a large mismatch and decoupling between the substrate and overlayer states, effectively isolating the bulk Cu valence states from the surface. This isolation means that the Cu indirect emission now originates from the interface (rather than the surface), and is thus reduced because of the reduced $\nabla \cdot \mathbf{A}$ at the interface.

Our photoemission experiment was carried out at the Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, Wisconsin. A small hemispherical analyzer with a ±1.5° acceptance cone was used to collect the data. The synchrotron beam was *p* polarized and had an angle of incidence of 45°. A normal-emission geometry was used. The Cu(100) substrate was prepared by sputtering and annealing in the usual manner, and the final surface showed a very sharp $(1 \times 1)$ electron diffraction pattern. Ag was deposited by thermal evaporation, and the rate was monitored by a water-cooled quartz oscillator. The growth was along the (111) direction as verified by electron diffraction, in agreement with earlier investigations [3].

The three panels of Fig. 1 show some of our spectra taken with photon energies of 12, 13, and 14 eV, respectively. For each photon energy, we show a spectrum for the clean Cu(100) surface and spectra for Ag coverages of 1 and 2 monolayers (ML). For the 14-eV case (bottom panel), each spectrum shows a Fermi edge followed by a plateau at higher binding energy. This plateau is caused by indirect emission from the *sp* band. This indirect-emission plateau joins a peak at about 1.4 eV binding energy, which is the direct-transition peak from the Cu *sp* band [4]. At higher binding energies are the Cu 3*d* and

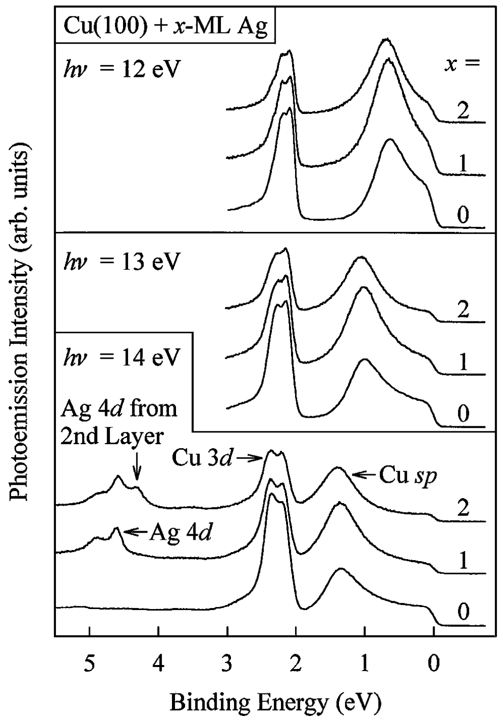

FIG. 1. Normal-emission spectra from clean Cu(100) and Cu(100) covered by 1 and 2 ML of Ag. The three panels correspond to spectra taken with photon energies of 12, 13, and 14 eV, respectively. The spectra in each panel are normalized in the same way, and the intensities are directly comparable.

Ag 4*d* features as labeled in the figure. These three spectra are normalized to the synchrotron beam current, and thus the relative intensities are directly comparable. The Cu 3*d* emission becomes weaker for increasing Ag coverages due to attenuation by inelastic scattering within the overlayer. The Ag 4*d* emission shows a pair of peaks at one monolayer coverage. When another monolayer of Ag is added onto the surface, the middle peak becomes more intense, and a new peak is observed on the lower binding energy side. If the coverage of the Ag is increased slowly from below a monolayer to over a monolayer, one can easily detect the onset of emission from this new peak, which signals the completion of the first monolayer and the beginning of the buildup of the second monolayer. This allows us to make an independent absolute determination of the coverage.

The spectra for the other two photon energies are very similar. The main difference is that the direct-transition peak is at a different binding energy. By moving this peak around, we can examine the behavior of the peak and its wings in greater detail. A qualitative visual inspection of the three sets of data yields the following observations. (i) The Fermi edge and the indirect-emission plateau are rather intense for the clean surface, but become significantly suppressed by Ag deposition. (ii) The direct-transition peak is rather asymmetric for the clean surface, with the wing on the right side being much higher than that on the left side. This asymmetry is reduced with Ag coverage, and the line shape becomes fairly symmetric at a Ag coverage of 2 ML. (iii) The peak height of the direct-transition feature is significantly increased with 1 ML Ag deposition, and is approximately restored to the clean-surface value with the deposition of the second monolayer of Ag. This behavior appears unusual because inelastic attenuation by the overlayer should cause a general reduction in intensity as seen for the Cu 3*d* emission.

The direct-transition peak for $h\nu = 13$ eV is located midway between the Fermi edge and the Cu 3*d* emission, allowing a detailed analysis of its line shape. Figure 2 shows amplified versions of these spectra. Again, these spectra are normalized, and the intensities are directly comparable. The vertical "*I* bars" under the peaks are used as a "meter stick" to highlight the variations in peak height and asymmetry as mentioned above. From perturbation theory the basic line shape is given by [2,5]

$$I(E) \propto \left| \frac{1}{E - E_0 - i\gamma/2} + C(1 + BE) \right|^2 . \tag{1}$$

In this equation, the first term represents the direct transition, where $E$ is the binding energy, $E_0$ is the center of the direct-transition peak, and $\gamma$ is the full width of the peak. The second term represents the indirect-transition

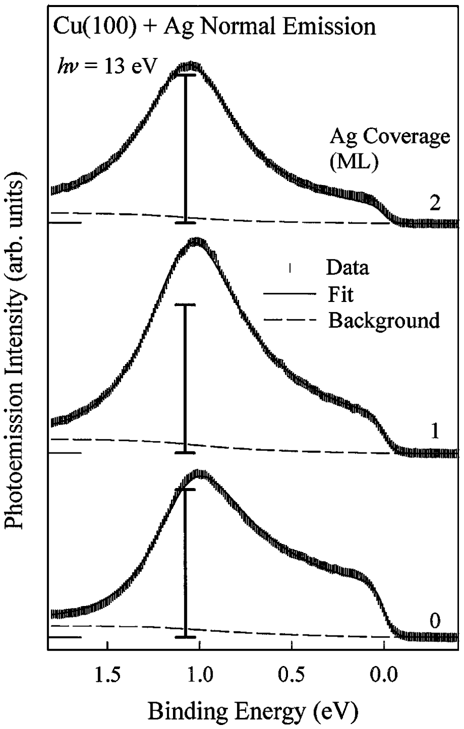

FIG. 2. Normal-emission spectra from clean Cu(100) and Cu(100) covered by 1 and 2 ML of Ag taken with a photon energy of 13 eV. The vertical "*I* bars" under the peaks are drawn at the direct-transition energy, and have the same height. They are used as a "meter stick" to highlight the variations in peak height and asymmetry. The dashed curves indicate the Shirley background function for each spectrum.

continuum. For the very limited energy range in our experiment, a linear approximation suffices. Thus, $B$ is the slope, and $C \propto \nabla \cdot \mathbf{A}$ is a complex number characterizing the relative amplitude of the indirect transition. The two amplitude terms in Eq. (1) add linearly, and interference between the two can lead to an asymmetric direct-transition peak. The effect of adding Ag onto the surface is to suppress the indirect transition as discussed above, and so $|C|$ should become significantly smaller. This should lead to a suppression of the interference effect and the asymmetry of the direct-transition peak.

Our data are analyzed using the following fitting function:

$$AT^n\left(1 + S\int_{-\infty}^{E} dE\cdot\right)\{[I(E)F(E)] \otimes G(E)\}. \qquad (2)$$

Here, the basic line shape function $I(E)$ from Eq. (1) is multiplied by a Fermi Dirac distribution function $F(E)$ to account for electron statistics, and then convoluted with a Gaussian $G(E)$ to account for instrumental broadening. A Shirley background function [6], which is proportional to the integral of the elastic spectrum with a proportionality constant $S$, is then added. Finally, each spectrum is multiplied by a normalization factor $AT^n$, where $A$ is an overall normalization factor, $T = 0.83$ is the layer attenuation factor for a Ag monolayer, and $n$ is the number of Ag monolayers on the Cu substrate. This layer attenuation factor is determined from an independent measurement of the mean free path in Ag (13 Å) at the appropriate kinetic energy [7], and is fairly close to the observed attenuation of the Cu $3d$ feature seen in Fig. 1. The fitting function in Eq. (2) is used to fit all three spectra in Fig. 2 simultaneously. The fitting parameters that are common for all three spectra are $A$, $B$, $S$, $E_0 = 1.077$ eV, $\gamma = 0.639$ eV, and an instrumental resolution of 0.034 eV (mainly determined by the sharpness of the Fermi edge). The fit also yields $C$ for each spectrum, and the results are $C = -0.550 - 0.773i$, $-0.519 - 0.002i$, and $-0.191 - 0.089i$ for $n = 0$, 1, and 2, respectively.

The fits are shown as curves in Fig. 2. The quality of the fit is quite good considering the small number of parameters used in the model (and the fact that the three spectra are fit simultaneously on the same intensity scale). The vertical $I$ bars mentioned above are drawn at the line center $E_0$, and it is clear that the interference effect can cause a significant shift in the apparent peak position (up to ~0.1 eV) and the apparent "center of gravity" of the peak (up to ~0.3 eV). This shift is something to watch out for when angle-resolved photoemission is employed for precise band mapping. The significant increase of the peak height in going from $n = 0$ to 1 despite the attenuation by the overlayer is well reproduced by the fit. The peak height for $n = 0$ is affected by destructive interference. This effect of destructive interference is reduced when Ag is added onto the surface, resulting in an increase in peak height.

From our fits, we find $|C|^2 = 0.90$, 0.27, and 0.044 for $n = 0$, 1, and 2, respectively. This quantity is proportional to the indirect emission intensity, and is indeed suppressed for increasing $n$ as noted above. By $n = 2$, this is reduced to about 5% of the clean-surface value. We do not expect this to reduce to zero because Ag and Cu are after all not perfectly matched in terms of their dielectric properties. However, this is a substantial reduction and makes the interference effect much less apparent. The resulting direct-transition peak appears quite symmetric to the eye as seen in Fig. 2. Note that the screening length is rather short in metals, and by $n = 2$, the interface is already well shielded from the surface. Data for higher Ag coverages do not show much further change in line shape. The direct-transition peak becomes rapidly attenuated, and eventually, Ag-derived features including a surface state and quantum-well peaks appear in the spectra [8,9].

To summarize, this experiment is a direct test of the effect of surface photoemission in Cu(100). This surface, when clean, shows a rather asymmetric direct-transition peak due to interference with surface-induced indirect emission. If this asymmetry were associated with the bulk properties only, it would have been unaffected by an overlayer, and the peak intensity would just have been attenuated. Experimentally, we find that a thin Ag overlayer removes this asymmetry, and this sensitivity to surface boundary condition demonstrates the surface origin of this effect. The peak height associated with the direct transition shows a nontrivial variation as a function of Ag coverage. All of these observations are explained naturally in terms of a suppression of the indirect emission channel that arises from a dielectric mismatch at the boundary. The basis of our analysis was Eq. (1), a simple and yet fairly general formula that will be useful in future studies of line shapes. Its utility in angle-resolved photoemission is similar to that of the well known Doniach-Šunjić line shape [1] in core-level analysis.

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