Probing the Wave Function of a Surface State in Ag(111): A New Approach

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The envelope function of a surface state in Ag(111) has been determined with a new experimental approach on the concept that spatially varying physical quantities near the surface can be probed in real space with the use of samples with tailored atomic configurations. Samples of Ag(111) with one near-surface atomic layer replaced by a closely matched Au atomic layer were fabricated by molecular-beam epitaxy.

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With modern materials-synthesis techniques, such as molecular-beam epitaxy, it is possible to fabricate solid samples with precisely controlled structures. This development opens up new opportunities to investigate selectively certain material properties by use of samples with tailored configurations. This paper demonstrates this experimental approach in a simple model system.

The subject of study is the wave function of surface electronic states. For a solid occupying the half-space $z \geqslant 0$, the wave function of a surface state localized near $z = 0$ has the general form

$$\psi(\mathbf{r}) = u(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r} - \beta z), \qquad (1)$$

for $z > 0$.[1] The function $u(\mathbf{r})$ is periodic if surface relaxation (small in most cases) is ignored. The term $\exp(-\beta z)$, with $\beta > 0$, is the envelope function of the surface state; the parameter β^{-1} (decay length) determines the degree of localization. If surface relaxation is not negligible, the envelope function of ψ should include the layer-to-layer variation in $u(\mathbf{r})$ in the region of nonzero relaxation. The experiment to be described below determines the envelope function of $|\psi|^2$ in real space.

The surface chosen for the present study is Ag(111) which has a surface state at the two-dimensional Brillouin zone center.[2-4] Figure 1 shows the approximate bulk band dispersions of Ag near the Fermi level E_F for the wave vector k along the $\langle 111 \rangle$ direction.[4-7] The surface state lies within and near the lower edge of the forbidden gap between the L_4^- and L_4^+ critical points.[4] To probe the wave function of this Ag(111) surface state at a given atomic plane below the Ag(111) surface, a small perturbation in the crystal potential is artifically introduced locally by fabrication of an Ag(111) sample with that particular Ag atomic layer replaced by a well-matched Au atomic layer. The perturbation, being small because Ag and Au have very similar valence electronic structures, causes a small shift in the surface-state binding energy, which is proportional to the expectation value of the localized perturbation to the lowest order. By a systematic change in the distance between the substitute Au atomic layer and the sample surface, the z dependence of the envelope function of $|\psi|^2$ can be mapped out directly from the measured energy shifts, from which the value of β can be obtained.

The parameter β is sensitively related to the boundary condition at the solid-vacuum interface, and is an important quantity characterizing the surface.[1] It is also related to the energy splitting of the surface state from the corresponding bulk continuum (δE, indicated in Fig. 1). The present technique is the only direct, real-space approach which has been developed to measure β.[8,9]

The photoemission measurements were performed at the Synchrotron Radiation Center of the University of Wisconsin–Madison. Synchrotron radiation from the Tantalus storage ring, monochromatized by the Mark-V grasshopper monochromator, was used as the

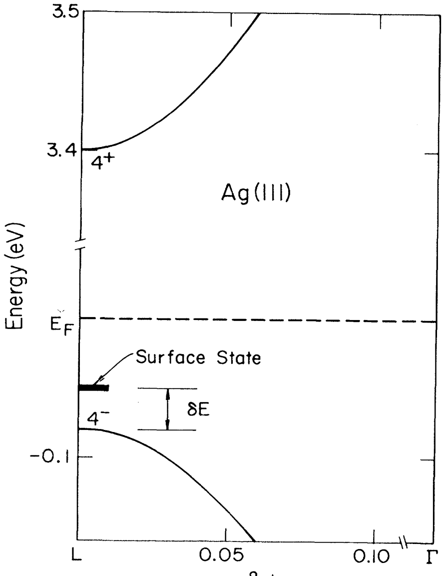

FIG. 1. Approximate bulk band dispersions of Ag near the Fermi level E_F for the wave vector k along the $\langle 111 \rangle$ direction from L to Γ. The energy of the surface state for Ag(111) within the gap is indicated.

light source. The photoelectrons were analyzed by a hemispherical analyzer with a full acceptance angle of 3°. The Ag(111) substrate was prepared by means of sputtering with Ar^+ and annealing in the usual manner. Ag(111) samples with one specific (111) atomic layer below the surface replaced by an equivalent Au atomic layer were prepared by molecular-beam epitaxy. It was demonstrated by electron diffraction, core-level photoemission studies, and ion-scattering studies that Au-Ag(111) interfaces formed at room temperature are abrupt with little strain and few stacking faults, and that the overlayers are smooth without clumping.[10-12] High-energy electron diffraction from all samples showed sharp unreconstructed (1×1) patterns. The surface cleanliness was verified with Auger spectroscopy.

Some of the photoemission spectra taken with a photon energy on $h\nu = 22$ eV and a normal-emission geometry are shown in Fig. 2 for various sample configurations as labeled. The binding-energy scale is referred to the Fermi level E_F. The sole peak in the spectra is the surface-state peak[2,3]; its width is dominated by the instrumental broadening. The vertical dashed line in Fig. 2 indicates the center position of the surface-state peak for clean Ag(111). The bulk states do not contribute significantly to the spectra because direct transitions from these states are not allowed.[13] The surface state of Ag(111) is seen to shift somewhat with the coverage of one monolayer of Au. This shift relative to clean Ag(111) becomes gradually reduced with increasing coverage of Ag over the Au monolayer. In other words, the binding-energy shift induced by the Au monolayer is a monotonically decreasing function of the distance between the sample surface and the (buried) Au monolayer. At very large coverages of Ag over the Au monolayer (e.g., the top spectrum in Fig. 2), the surface-state peak is essentially back at the same position as that of the starting clean Ag(111) surface.

The inset in Fig. 3 depicts the sample structure. The experimental binding-energy shifts relative to clean Ag(111) are plotted in Fig. 3 as circles for different Ag overlayer thicknesses t on top of the Au monolayer initially laid down in the Ag(111) substrate. The binding-energy shifts were determined by a shift of the spectra relative to that for clean Ag(111) until optimum alignment of the line shapes was obtained. This was done either by use of a computer routine or by visual inspection; both methods yielded essentially identical results. The estimated error for the binding-energy shifts is ±10 meV.

We now describe our theoretical model. The inset in Fig. 3 shows schematically the perturbation in crystal potential ΔV caused by the substitute Au mono-

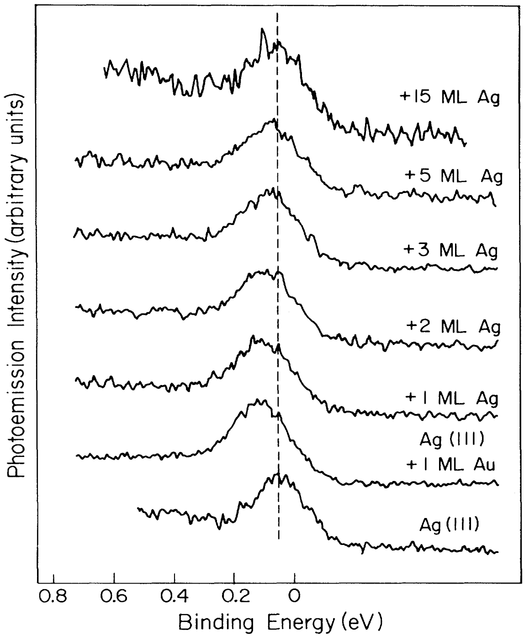

FIG. 2. Photoemission spectra from Ag(111) taken with a photon energy of $h\nu = 22$ eV and a normal-emission geometry. The spectra are for, from bottom to top, clean Ag(111), Ag(111) + 1 ML Au, and Ag(111) + 1 ML Au + 1, 2, 3, 5, and 15 ML of Ag, respectively. ML stands for monolayer.

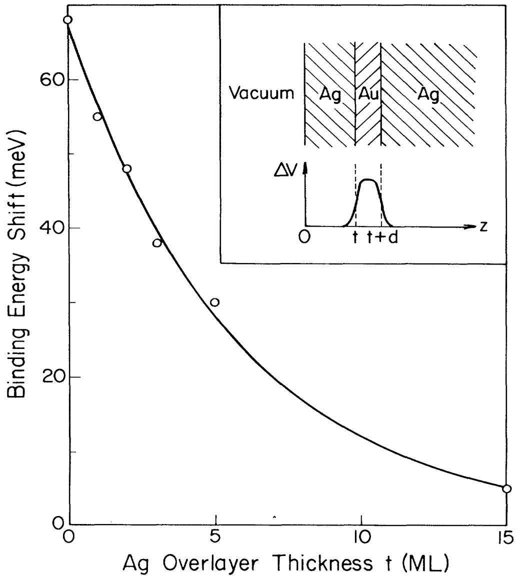

FIG. 3. Experimental binding-energy shifts (circles) for the surface-state peaks seen in Fig. 2 relative to clean Ag(111) for various Ag overlayer thicknesses t on top of the Au monolayer. The solid curve is a least-squares fit. The inset shows schematically the sample configuration and the perturbation in crystal potential ΔV as a function of z.

layer. ΔV is highly localized and is significant only within $t \leq z \leq t+d$, where t is the Ag overlayer thickness and $d=2.36$ Å is the interlayer spacing for Ag(111) and Au(111); this high degree of localization is a result of the extremely short screening lengths in metals. With the usual first-order perturbation theory, the shift in the Ag(111) surface-state binding energy is given by

$$\Delta E(t) = \langle \psi | \Delta V | \psi \rangle, \qquad (2)$$

where ψ is the normalized unperturbed wave function of the Ag(111) surface state of the form given by Eq. (1). From Eqs. (1) and (2) and the fact that ΔV is highly localized, we obtain

$$\Delta E(t) = \Delta E(0) \exp(-2\beta t), \qquad (3)$$

assuming $u(\mathbf{r})$ to be exactly periodic and $\beta^{-1} >> d$ (these assumptions will be verified below). The term $\exp(-2\beta t)$ is just the envelope function of $|\psi|^2$. The solid curve in Fig. 3 is the result of a least-squares fit to the data points using Eq. (3), with $\Delta E(0)$ and β as the only fitting parameters. The parameter β^{-1} (decay length) from the fit is equal to 11.7 interlayer spacings. Thus the condition $\beta^{-1} >> d$ for Eq. (3) to be valid is satisfied. The fit in Fig. 3 describes the data well, indicating that surface-relaxation effects causing layer-to-layer variation in $u(\mathbf{r})$ are indeed negligible.

It is interesting to note that β^{-1} is very large compared with the atomic dimensions. Modern self-consistent calculations of surfaces are often performed for a slab geometry with a slab thickness typically less than ten monolayers. Much thicker slabs are clearly needed for an accurate calculation of the surface properties of Ag(111). No theoretical values of β for the surface state under consideration exist in the literature.

We now comment on whether or not it is adequate to use the *nondegenerate* first-order perturbation theory [see Eq. (2)] in the present case. The energy splitting of the surface state from the L_4^- critical point, δE (see Fig. 1), is given quite accurately by

$$\delta E = \hbar^2 \beta^2 / 2m^*, \qquad (4)$$

where m^* is the effective mass associated with the lower bulk band shown in Fig. 1 and is about 0.17 times the free-electron mass.[5] With our experimental value of β, we obtain $\delta E = 30$ meV. Most of the data points in Fig. 3 correspond to binding-energy increases greater than 30 meV, meaning that the resulting states are actually pushed down to within the energy range of the bulk continuum for the semi-infinite Ag(111) substrate. The original surface state is thus mixed with the bulk states to become a *surface resonance*, and the nondegenerate perturbation theory is not rigorously applicable in the present case. The situation is quite similar to the familiar autoionization phenomenon in atomic physics.[14] We have evaluated the degree and effect of mixing between the bulk and surface states by calculating the redistribution of oscillator strength within the effective-mass approximation. The calculation is sufficiently involved to warrant a separate publication; here we shall only describe the major results. The mixing causes a dilution of the original surface state into many states with an effective band width quite small compared with our instrumental width and hence not clearly noticeable in our spectra. One can also show, quite independent of the effective-mass approximation, that the integrated oscillator strength is preserved and that the center of gravity of the oscillator strength is still given by the nondegenerate first-order perturbation theory despite the mixing. Equation (3) is therefore still valid (with β^{-1} being the decay length of the *unperturbed* surface-state wave function as before) provided that $E(t)$ is now interpreted as being the line center of the (slightly broadened) surface-resonance or surface-state peak. Our data analysis discussed above also remains valid.

Note that the above model is based on a first-order perturbation calculation in which the *unperturbed* wave function is used. The second-order correction is small. The ratio between the second- and first-order effects can be easily estimated to be given by the product of two factors: one factor being $2\beta d \simeq \frac{1}{6}$ and the other factor being the fractional difference between the Ag and Au crystal potentials. The latter factor depends somewhat on the theoretical model, but is no larger than about 10%. Thus the second-order correction is indeed negligible in the present case.

Another related issue which has been discussed frequently in recent years concerns the work-function change induced by adsorption. Within our model, both the work-function change and the surface-state shift are consequences of the change in crystal potential due to the replacement of Ag by Au. The work-function change, being an interesting quantity, merits a separate publication; it does not significantly affect our calculation. All data points in Fig. 3 correspond to samples with essentially the same work function except the left-most data point [Au monolayer on Ag(111), which has a work function different by about 10%]. The Ag(111) surface-state wave function penetrates only slightly into the vacuum with a decay length of about 0.9 Å.[1] For comparison, the decay length below the surface is 28 Å. Thus the probability of one's finding the electron associated with the surface being outside the surface is only of the order of 3%. The uncertainty in our calculation due to the work-function change is no larger than about 10 meV for the left-most data point in Fig. 3, and is negligibly small for the rest of the data points. Since β is obtained from a fit to all of the data points, the work-function change should have little effect on our calculation.

In summary, the present experiment demonstrates a new experimental approach based on the concept that spatially varying physical quantities near the surface can be probed in real space with the use of samples with tailored atomic configurations. The envelope function of a surface state in Ag(111) has been determined. The present approach is applicable to many other well-behaved epitaxial systems[15] as well as to the studies of other physical properties (other than the decay length).[16]

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[15] We also have preliminary data for a similar surface state in Au(111); the experimental value of β^{-1} obtained with the same method of analysis is about 3.3 interlayer spacings, in excellent agreement with the result of a recent self-consistent slab calculation [S. H. Liu *et al.*, J. Electroanal. Chem. **176**, 325 (1984)]. Since β^{-1} is really not much larger than d, this system may not be described accurately by our model.

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