RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 6 15 MARCH 1985

Unoccupied surface resonance on Cu(100) and the effect of vacuum-level pinning

D. P. Woodruff,* S. L. Hulbert, and P. D. Johnson
Physics Department, Brookhaven National Laboratory, Upton, New York 11973

N. V. Smith
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 14 December 1984)

We have identified a new unoccupied surface resonance approximately 1.15 eV above the Fermi level on Cu(001) with the use of inverse photoemission. The resonance has to be separated from a nearby intense peak due to a bulk direct transition. This has been done in two ways: (1) varying the photon energy, which causes a shift in the bulk peak, and (2) varying the work function, which causes a shift in the resonance. The occurrence of the resonance is consistent with a recently proposed phase analysis.

Occupied surface localized states both inside and outside bulk band gaps (known, respectively, as surface states and surface resonances) have been identified on many surfaces using angle-resolved photoemission. More recently, k-resolved inverse photoelectron spectroscopy (KRIPES) has been used to show that not only unoccupied surface states can be detected within bulk band gaps, but also states derived from the image potential experienced by an electron near the surface.[1-5] These latter states lie outside the surface and are far less localized due to the long-range nature of the image potential. Recently, Hulbert *et al.*[5] have shown that a simple picture of multiple reflection between the image potential barrier and the barrier of the crystal gap may be used to determine the conditions for bound states at the surface.[6,7] Furthermore, this model was found to account successfully for the energy location of the unoccupied image potential states on Cu(111) and Cu(100) and of the occupied surface state on Cu(111). Here, we show that an unoccupied surface resonance, predicted to occur on Cu(100) by this same model,[5] is indeed observed, and that the dependence of its energy location on the work function can also be accounted for.

Figure 1 reproduces the theoretical results of Hulbert *et al.* as applied to Cu(100). The electron at the surface suffers a phase change of ϕ_B on reflection at the image potential barrier and a phase change of ϕ_C on reflection at the crystal surface. Bound or surface states are determined by the condition[7]

$$\Phi = \phi_C + \phi_B = 2\pi n, \quad n = 0, 1, 2 \ldots . \tag{1}$$

In particular, for a total phase shift of zero, the bound state is known to be a surface state or surface resonance, while a phase shift of 2π corresponds to the first state in a Rydberg series of image potential states. Figure 1 shows that the energy at which the total phase is zero falls below the bottom of the bulk band gap at X_4, and so indicates that the localized state should be a surface resonance. The observation of this state has not previously been reported but the fact that it lies within a bulk band means the identification is less simple than for a gap state. Moreover, most KRIPES studies have so far been performed at the fixed photon energy of 9.7 eV. At this energy and normal incidence a strong direct transition is seen to a bulk band state some 0.4 eV above the Fermi level, complicating the identification of the surface resonance at about 1.2 eV above the Fermi level. Nevertheless, with hindsight, some evidence for this feature is seen in early data as a marked asymmetry of the peak attributed to the direct transition.[8]

Using a new type of photon detector, based on the chromatic aberation properties of a LiF lens, KRIPES data in the isochromat mode can be collected at different photon energies in the range 8–11.7 eV.[9] Figure 2 shows normal incidence spectra collected at three different photon energies from a clean Cu(100) surface. As the photon energy increases, the main peak due to the bulk band direct transition shifts towards the Fermi level in keeping with the known dispersion of the initial- and final-state bands; indeed, at the highest photon energy (11.0 eV) the direct transition is actually forbidden and the peak seen at E_F is a reflection of the limited momentum resolution in the present experiment. Through this photon energy range the weak asymmetry seen in the lowest photon energy data emerges as a distinct shoulder. Using a fitting routine

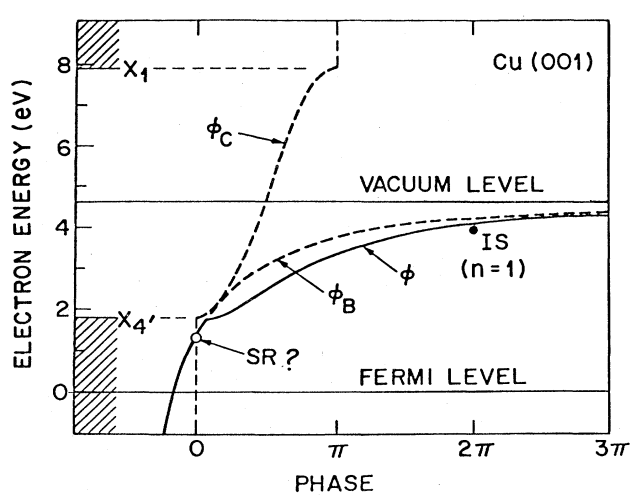

FIG. 1. Energy dependence of the phases ϕ_C, ϕ_B, and the total phase $\phi_C + \phi_B$ which appear in the multiple reflection theory of surface states for Cu(100). The filled circle (IS) indicates the observed binding energy of the $n = 1$ image potential state. SR indicates the energy of the crystal-induced surface resonance required by the model.

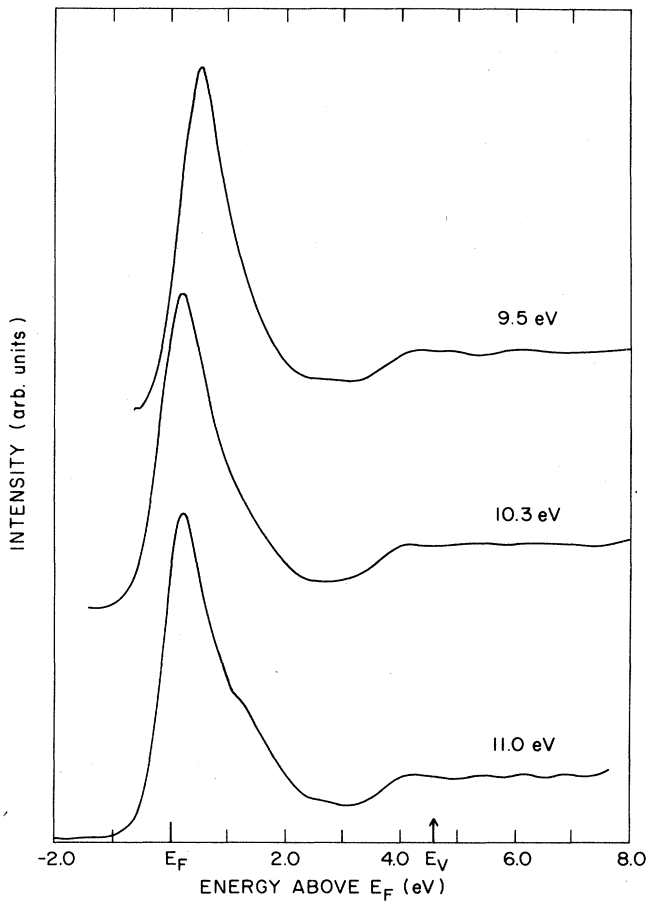

FIG. 2. Normal incidence k-resolved inverse photoemission spectra taken on Cu(100) as a function of the energy of photon detection.

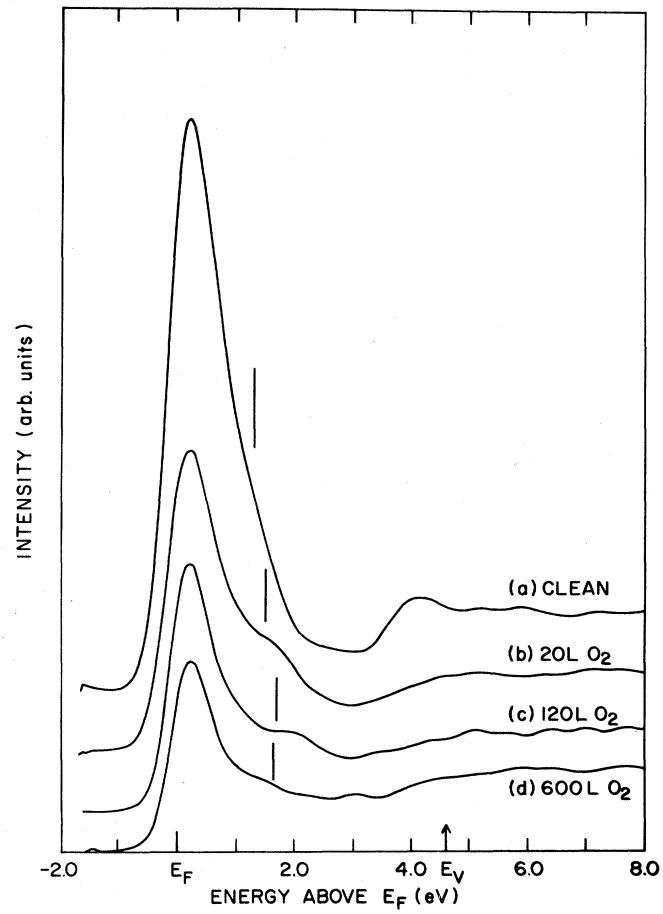

FIG. 3. Normal incidence k-resolved inverse photoemission spectra taken on Cu(100) following the indicated exposures of oxygen. The corresponding measured work function changes in these spectra are (a) $\Delta\phi=0$, (b) $\Delta\phi=140$ mV, (c) $\Delta\phi=330.5$ mV, and (d) $\Delta\phi=305$ mV. The position of the $n=0$ condition in formula (1) is indicated by markers for the different work functions. E_v indicates the vacuum level on the clean surface.

which employs superposition of Lorentzian distributions for the bulk transition and surface resonance convoluted with a Fermi function we are able to establish that the resonance is approximately 1.15 eV above the Fermi level, close to the 1.2-eV value predicted by the model.

Figure 3 shows the result on the normal incidence KRIPES spectra of exposing the clean copper surface to oxygen at room temperature. Under these conditions it is known that as the oxygen coverage increases, the work function increases by a maximum amount of ≈ 300 meV at a coverage of about 0.5 monolayers and then subsequently decreases. At room temperature this maximum work function change occurs at ≈ 150–200 L (1 L=1 Langmuir $=10^{-6}$ Torr sec) exposure.[10] However, no ordered overlayer structure is found under these conditions although with considerably greater exposures (≈ 1000 L) a poor $c(2\times 2)$ LEED pattern is seen. Figure 3 shows that the intensity of the direct transitions falls rapidly as oxygen is adsorbed; the same effect is seen in photoemission for the s-p band direct transition[11] and can probably be attributed to loss of $k_{\parallel}$ conservation on the disordered surface for this strongly dispersing feature. Figure 3 also shows that while the image potential state (≈ 3.8 eV above E_F) is strongly quenched by oxygen adsorption, the surface resonance feature moves to higher energy before itself becoming quenched. This observation that the feature is eventually quenched on increased oxygen adsorption rules out the possibility that at low coverages we are merely observing some antibonding level derived from the oxygen. The work function changes were measured using a retarding potential method and good agreement was found between the present experiment and the previously published work function changes of Hoffman, Unwin, Wyrobisch, and Bradshaw.[10] The markers on Fig. 3 show the predicted position of the surface resonance on the clean surface, and the position on the oxygen-exposed surface if this feature tracks the vacuum level and therefore shifts by amounts equal to the work function change. This behavior is exactly that to be expected from the model of Hulbert *et al.*,[5] as may be seen in Fig. 1. For a surface resonance there is no contribution to the total phase shift from ϕ_C, so as the vacuum level is raised the full phase shift function (ϕ_B only) shifts at exactly the same rate. The data of Fig. 3 therefore appear to provide further evidence for this simple model for all types of sur-

face state. One interesting feature of the data is that it appears that the image potential state is far more readily suppressed by the adsorption of oxygen than the surface resonance. The fact that the image potential state on this surface does appear to be reasonably clearly resolved with a $c(2\times2)$ overlay of chlorine,[3] however, suggests that it may be due to the sensitivity of the image potential state to surface order. For that system the image potential state was also observed to track, at least approximately, the vacuum level. This is broadly compatible with the model illustrated in Fig. 1. Although the image potential state corresponds to the total phase $\phi_B+\phi_C=2\pi$, and a change of vacuum level shifts only the ϕ_B component, the weak energy dependence of $\phi_B+\phi_C$ at values close to 2π means that the deviation of image potential state movement relative to the work function change will be small.

In conclusion, we have shown not only that predictions of the simple model of Hulbert *et al.*[5] [that an unoccupied surface resonance occurs on Cu(100)] is correct, but that this model is also able to account for the pinning of this state in energy relative to the vacuum level. Indeed these experiments suggest that surface states of the Shockley type will in general be related to the vacuum level via the image potential, a result that was suggested by Shockley in his original paper.[12]

We would like to acknowledge the assistance of R. J. Garrett with the fitting programs. This work was supported in part by the Division of Materials Sciences, U.S. Department of Energy, through Contract No. DE-AC02-76CH00016.

*Permanent address: Physics Department, Warwick University, Coventry CV4 7AL, England.

[1]P. D. Johnson and N. V. Smith, Phys. Rev. B **27**, 2527 (1983).

[2]D. Straub and F. J. Himpsel, Phys. Rev. Lett. **52**, 1922 (1984).

[3]V. Dose, W. Altmann, A. Goldmann, V. Kolac, and J. Rogozik, Phys. Rev. Lett. **52**, 1919 (1954).

[4]D. A. Wesner, P. D. Johnson, and N. V. Smith, Phys. Rev. B **30**, 503 (1984).

[5]S. L. Hulbert, P. D. Johnson, N. G. Stoffel, W. H. Royer, and N. V. Smith, Phys. Rev. B (to be published).

[6]E. T. Goodwin, Proc. Cambridge Philos. Soc. **35**, 205 (1939).

[7]P. M. Echenique and J. B. Pendry, J. Phys. C **11**, 2065 (1978).

[8]D. P. Woodruff, N. V. Smith, P. D. Johnson, and W. A. Royer, Phys. Rev. B **26**, 2943 (1982).

[9]T. T. Childs, W. A. Royer, and N. V. Smith, Rev. Sci. Instrum. (to be published).

[10]P. Hofman, R. Unwin, W. Wyrobisch, and A. M. Bradshaw, Surf. Sci. **72**, 635 (1978).

[11]D. T. Ling, J. N. Miller, D. L. Weissman, P. Pianetta, P. M. Stefan, I. Lindau, and W. E. Spicer, Surf. Sci. **95**, 89 (1980).

[12]W. Shockley, Phys. Rev. **56**, 317 (1939).