PHYSICAL REVIEW B VOLUME 28, NUMBER 4 15 AUGUST 1983

Observation of a new surface state on Cu(001)

S. D. Kevan
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 31 May 1983)

High-resolution angle-resolved photoemission studies of the Cu(001) surface demonstrate the existence of a surface state which has not previously been reported. The state is located in a relative bulk band gap near the Fermi energy at the $\bar{X}$ point of the two-dimensional Brillouin zone. Its energy position and dispersion are in excellent agreement with recent calculations for this surface. Comparisons are made of this state's natural energy width and dispersion with similar states on other copper surfaces.

Over the past decade, copper surfaces have provided an ideal testing ground for comparisons between angle-resolved photoemission (ARP) studies and first-principles calculations of surface electronic structures. Numerous experimentally observed surface-state dispersions[1-4] are in semiquantitative accord with calculated results.[5-8] This paper reports high-resolution ARP studies of the Cu(001) surface which indicate the existence of a surface state which has not been reported previously. This state is located near the Fermi energy at the $\bar{X}$ symmetry point of the two-dimensional Brillouin zone. Very good energy and momentum resolution were required not only for an accurate characterization of this state but also merely to detect its existence. Numerous earlier studies failed in both respects.[3,4,9-17] Further, a promising level of agreement between the experimentally derived dispersion relation and that of recent self-consistent calculations[8] is reported. The importance of such high-resolution ARP studies combined with self-consistent calculations is thus emphasized in the present studies.

Experiments were performed in an ARP spectrometer described elsewhere.[18] As indicated earlier, an important aspect of the present spectrometer is its emphasis on very high energy and angular resolution. The work reported here was performed using an energy resolution of 20–25 meV, and an angular resolution of 0.6°, both full width at half maximum. The Cu(001) crystal was the same as that used previously and was prepared in a similar fashion.[19] A prolonged high-temperature sputter had the effect of decreasing the fundamental momentum broadening[19-21] from the value reported previously (~ 0.03 Å^{-1}) to ~ 0.02 Å^{-1}. This is presumably due to a reduction of the residual sulfur impurity concentration, although no impurities were detectable using Auger electron spectroscopy either before or after this treatment. The experimental momentum resolution was small compared to this fundamental contribution. The crystal yielded sharp low-energy electron diffraction spots having a width of less than 1° and was aligned by *in situ* electron diffraction and laser autocollimation. Resonance radiation was incident at 45° from the sample normal in the ΓLUX plane of the bulk Brillouin zone, and the electronic momentum parallel to the surface, $\vec{k}_{\parallel}$, was varied by rotating the electron energy analyzer in that plane (see Fig. 1).

ARP energy distribution curves for $\vec{k}_{\parallel}$ near the $\bar{X}$ point of the two-dimensional Brillouin zone are shown in Fig. 1 for the clean surface and after exposure to 50-L (1 L = 10^{-6} Torr sec) O_2. The surface state is seen as a sharp peak very close to the Fermi energy, E_F, while the larger feature at $E_B \sim 0.5$ eV arises from a bulk momentum-conserving transition and has been described in detail elsewhere.[19] As is seen in the figure, the surface state is quenched while the bulk state is virtually unchanged by the exposure to oxygen. This surface state seems to be more sensitive to contamination than other copper surface states.[2-4] presumably due to its location near E_F.

While the state was observable at $\bar{X}$ at three photon energies, the close proximity of the broader bulk feature at Ne I($h\nu = 16.85$ eV) and He I($h\nu = 21.22$ eV) makes studies at Ar I($h\nu = 11.85$ eV) more accurate. These results are shown in Fig. 2, where the region near E_F is shown under high resolution at 1° intervals. Several important features are apparent. The maximum binding energy is 58 ± 5 meV, implying that at room temperature the state at $\bar{X}$ has a 90% probability of being occupied due to thermal smearing of the

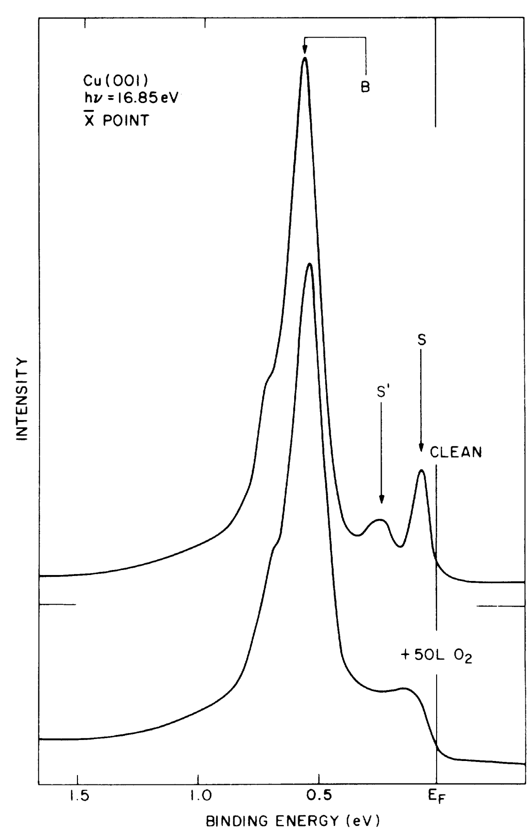

FIG. 1. Energy distribution curves (EDC's) of the Fermi-level region near $\bar{X}$. Top: clean surface; bottom: after contamination. S is the surface-state peak; S' is the same, excited by the Ne I satellite line; B is a bulk feature.

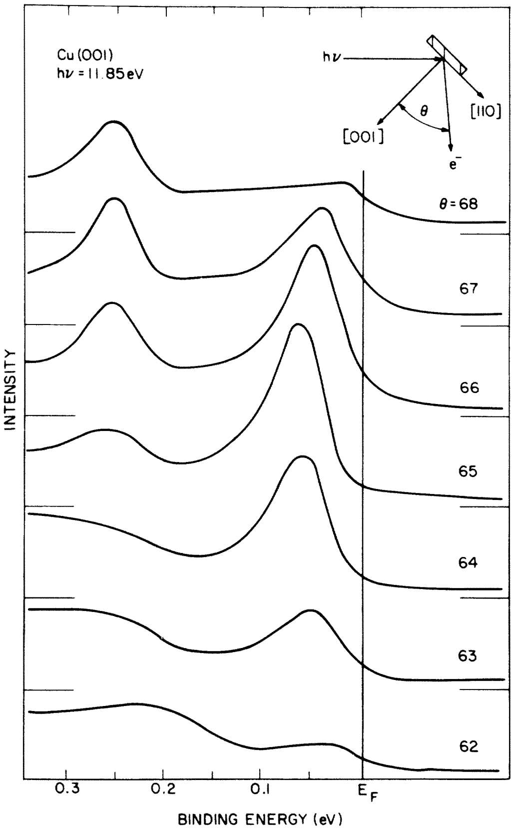

FIG. 2. High-resolution EDC's of the surface-state region.

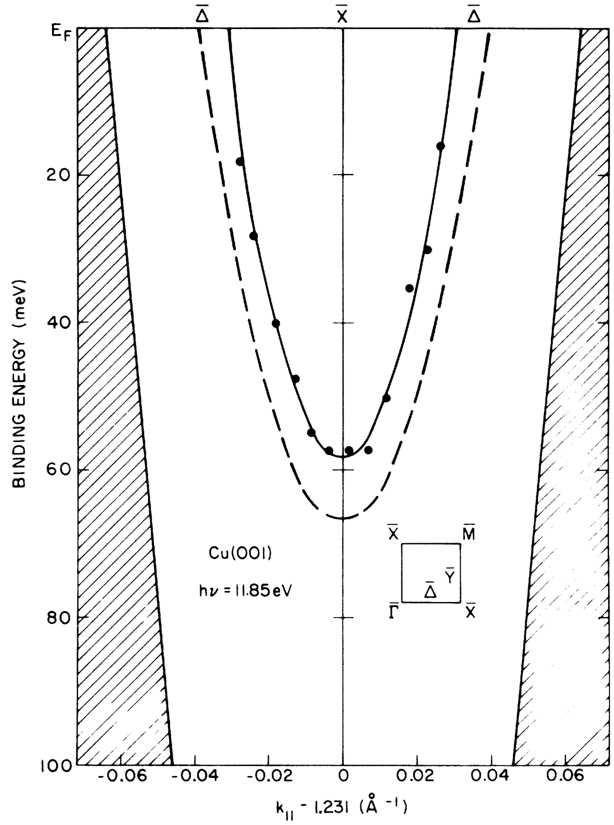

FIG. 3. Surface-state dispersion relation. Solid curve is a parabolic fit to the experimental points, while the dashed curve is the calculated dispersion relation. Shaded region is the experimental projected bulk continuum.

Fermi level. The measured width at this point is ~50 meV, while the width extrapolated to zero resolution is ~30 meV. This state competes[3] for being the sharpest feature observed in condensed-state ARP studies. The effect of the Ar I doublet line at $h\nu = 11.65$ eV is also clearly apparent. At these oblique emission angles, the observed dispersion relations for the two photon energies of the doublet are shifted from each other by 2°–3°. This explains the apparent change in branching ratio for the two peaks observed in the figure. Finally, the excursion of the surface state below E_F occurs over an angular range of ~4°, corresponding to a momentum space width of ~0.06 Å^{-1}. This fact, along with the sharpness and small integrated intensity of the peak, clearly explains why previous studies did not observe this state, and indicates the utility of such high-resolution studies.

The dispersion of the peak with parallel momentum can be discerned by inspection of Fig. 2. Due to the interference of the Fermi level, however, the peak must be least-squares fitted to a Lorentzian folded with a Fermi function to produce an accurate dispersion relation. The results of such an analysis are shown in Fig. 3. Also shown in the figure is a parabolic least-squares fit to the experimental points. This yields

$$E(k_\parallel) = 57.0(k_\parallel - 1.231)^2 - 0.058 \ ,$$

with E in eV and $k_\parallel$ in Å^{-1}. A small linear term due to sample misalignment has been removed from this relation by shifting the experimental momenta by < 0.01 Å^{-1}. The effective mass of the fitted relation, $m^* = (0.067 \pm 0.01) M_e$, is quite small compared to other noble-metal surface states.[1,2]

Also shown in Fig. 3 is an *experimental* projected bulk continuum. An interpolation calculation[22] indicates that the lower edge of this continuum corresponds to band 6 along the [110] axis, reflected about the $\bar{X}$ point. Over the limited momentum range of this experiment, the continuum can be deduced fairly accurately by a linear extrapolation of the values of $k_F = 1.293$ Å^{-1} and $v_F = 7.24$ eV/Å^{-1} from Fermi-surface studies.[23] The value of the bulk continuum edge at $\bar{X}$ is then just $E_{\bar{X}} = (k_F - k_{\bar{X}}) v_F = 0.45$ eV. The bulk continuum edge shown in Fig. 3 is two lines joining the Fermi-level crossings with this $\bar{X}$ point energy. Alternatively, one could use a measured dispersion relation for band 6 along the [110] axis[24]; this gives virtually identical results. The important conclusion of this exercise is that the surface-state dispersion exists entirely within a projected bulk band gap, at least below the Fermi level, lending further support for its identification as a true surface state.

There is an interesting contrast between this state and other qualitatively similar states on Cu(111) (Ref. 20) and Cu(011).[21] All three states show parabolic dispersion about a symmetry point in the respective two-dimensional Brillouin zones. However, unlike the other two surfaces, the bulk continuum edge from which the Cu(001) state is split is not simply parabolic. Indeed, since the point on the [110] axis which projects into the $\bar{X}$ point is not a symmetry point of that axis, there is a cusp in the lower bulk continuum edge at $\bar{X}$.

The final aspect of Fig. 3 is the dispersion relation for an X_1 symmetry surface state predicted in a recent self-consistent slab calculation of Cu(001).[8] The agreement between experiment and theory is unprecedented in similar computational efforts. The energy at the symmetry point and the effective mass differ by only 10 meV and 25%, respectively. Part of the slight discrepancy in the mass may be due to systematic errors in the fitting procedure used on the EDC's. This excellent overall agreement may be fortuitous in part; an older self-consistent calculation[6] fails to predict this surface state at all. Further calculations investigating the sensitivity to various input parameters would be useful.

A more serious discrepancy between both calculations and these experiments concerns the prediction of various low-lying surface states near $\bar{X}$. In particular, a state is predicted at ~4.5-eV binding energy at $\bar{X}$ in a projected band gap ~1 eV wide. No evidence for such a surface state was found in the present studies. On Cu(111), a low-lying surface state at $\bar{\Gamma}$ is also not observed at low photon energy, but becomes clearly visible near $h\nu = 70$ eV.[25] A more detailed, frequency-dependent experimental investigation of the (001) surface is in order.

In summary, a previously unobserved surface state on Cu(001) was reported. The state was found to exist below E_F over a very limited momentum range near the $\bar{X}$ point. The experimentally determined energy and effective mass were in excellent agreement with those reported in recent self-consistent calculations.

ACKNOWLEDGMENTS

I wish to thank L. Kleinman for providing details concerning his recent calculations.

[1] P. O. Gartland and B. J. Slagsvold, Phys. Rev. B 12, 4047 (1975).
[2] P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Surf. Sci. 85, 263 (1979).
[3] P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. B 20, 3059 (1979).
[4] P. Heimann, J. Hermannson, H. Miosga, and H. Neddermeyer, Phys. Rev. Lett. 42, 1782 (1979).
[5] Joel A. Appelbaum and D. R. Hamann, Solid State Commun. 27, 881 (1978).
[6] J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. Lett. 42, 332 (1979).
[7] D. G. Dempsey and L. Kleinman, Phys. Rev. B 16, 5356 (1977), and references therein.
[8] Armando Euceda, D. M. Bylander, Leonard Kleinman, and Kenneth Mednick, Phys. Rev. B 27, 659 (1983).
[9] L. Ilver and P. O. Nilsson, Solid State Commun. 18, 667 (1976).
[10] R. Courths, V. Bechelier, B. Cord, and S. Hüfner, Solid State Commun. 40, 1059 (1981).
[11] P. O. Nilsson and N. Dahlbäck, Solid State Commun. 29, 303 (1979).
[12] D. E. Eastman, J. A. Knapp, and F. J. Himpsel, Phys. Rev. Lett. 41, 825 (1978).
[13] J. A. Knapp, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B 19, 4952 (1979).
[14] D. Westphal, D. Spanjaard, and A. Goldman, J. Phys. C 13, 1361 (1980).
[15] J. Stöhr, G. Apai, P. S. Wehner, F. R. McFeely, R. S. Williams, and D. A. Shirley, Phys. Rev. B 14, 5444 (1976).
[16] S. D. Kevan and D. A. Shirley, Phys. Rev. B 22, 542 (1980).
[17] M. Lindroos, H. Asonen, M. Pessa, and N. V. Smith, Solid State Commun. 39, 285 (1981).
[18] J. Tersoff and S. D. Kevan (unpublished).
[19] S. D. Kevan, Rev. Sci. Instrum. (in press).
[20] S. D. Kevan, Phys. Rev. Lett. 50, 526 (1983).
[21] S. D. Kevan (unpublished).
[22] N. V. Smith, Phys. Rev. B 19, 5019 (1979).
[23] M. R. Halse, Philos. Trans. R. Soc. London, Ser. A 265, 507 (1969).
[24] P. Thiry, D. Chandesris, J. Lecante, C. Guillot, R. Pinchaux, and Y. Petroff, Phys. Rev. Lett. 43, 82 (1979).
[25] S. G. Louie, P. Thiry, R. Pinchaux, Y. Petroff, D. Chandesris, and J. Lecante, Phys. Rev. Lett. 44, 549 (1980).