Unoccupied surface states in Cu(001)

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The energy versus momentum dispersion of empty electronic states in Cu(001) has been measured with $\vec{k}$-resolved inverse photoemission. Four different final bands are identified. Theoretical calculations employing the one-step model of inverse photoemission prove that two of the four emission branches are due to bulk direct transitions while the remaining two are due to surface states of the Shockley and Tamm kinds, respectively.

The existence of electronic surface states on metals and semiconductors is now well established. While numerous investigations employing angular-resolved photoelectron spectroscopy have dealt with occupied electronic surface states,[1] experimental information on unoccupied surface states is still rather limited.[2–5] In particular, the energy versus momentum dispersion of such states has been measured in two cases only, namely, for surface states associated with the image potential on Cu(001) (Shockley type) and for volume split-off surface states (Tamm states) on Pd(111).[5] Subsequent measurements on Pd(111) (Ref. 6) failed to reproduce the results reported in Ref. 5. Despite continuing efforts,[7] the matter remains unresolved at present. In this paper, we present experimental inverse photoemission spectra for Cu(001). The data have been interpreted on the basis of theoretical calculations employing the one-step model of inverse photoemission.[8] Two bulk direct transitions and two surface states of the Shockley and Tamm type are identified on the $\bar{\Gamma}$–$\bar{X}$ high-symmetry line of the surface Brillouin zone.

The experimental setup used for the present measurements is described in detail elsewhere.[9] Very briefly, electrons from an electron gun mounted coaxially to a vacuum ultraviolet concave mirror impinge on the sample at an angle θ with respect to the surface normal. The radiation emitted by the sample is focused by the mirror into an energy selective Geiger-Müller counter with a 9.7-eV mean pass energy. The photon counter resolution is about 700 meV (full width at half maximum), and the overall energy resolution has been previously measured to be less than 900 meV.[10] The angular spread of the electron beam is smaller than 3° as inferred from the experimental data in Fig. 1.

A sample set of inverse photoemission spectra from Cu(001) as a function of θ, the angle of incidence in the ΓXUL mirror plane of the crystal ($\bar{\Gamma}$–$\bar{X}$ direction of the surface Brillouin zone) is shown in Fig. 1. The prominent emission feature just above the Fermi energy for normal incidence $\theta = 0°$ has previously been shown to be due to a bulk direct transition between bands 7 and 6.[11] The smaller steplike emission feature at about 4 eV has recently been shown to result from radiative transitions into surface states associated with the image potential.[4] Both of these emissions disperse to higher energy as the angle of incidence is increased, and the surface emission has vanished in the 27° spectrum. At $\theta = 30°$, a new emission peak emerges at 4.5 eV. This peak disperses to lower energies when θ is increased and finally splits off a fourth emission branch with a final-state energy of 5.2 eV at $\theta = 39°$. A collection of the experimental energy versus momentum dispersions for the four emission branches is shown in Fig. 2. Also included in Fig. 2 is the projected bulk band structure of copper.[12] Solid dots and open circles lie within the bulk bands and indicate bulk direct transitions. Open triangles refer to emission from transitions into image-potential surface states. Solid triangles denote the dispersion of the emission peak first observed in the 30° spectrum of Fig. 1. The latter falls in a gap of the projected bulk band structure and stays nearly parallel to the bulk band edge. It is thus a candidate for a surface resonance. An experimental test for the surface nature of this emission is its sensitivity to gas adsorption. The sample was exposed to 5 L (1 L = 10^{-6} Torr sec) of oxygen;

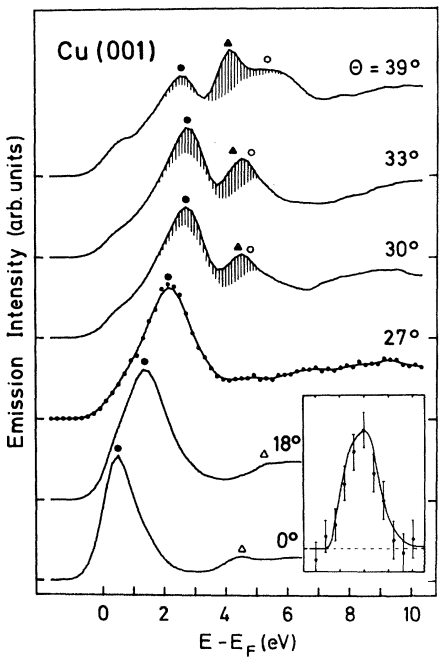

FIG. 1. Inverse photoemission spectra from Cu(001). The angle of incidence θ is varied in the ΓXUL mirror plane. Shaded areas indicate the attenuation of the clean sample spectra upon exposure to 5 L oxygen. The inset shows a difference spectrum from the region of surface-state emission compared with the experimental resolution function.

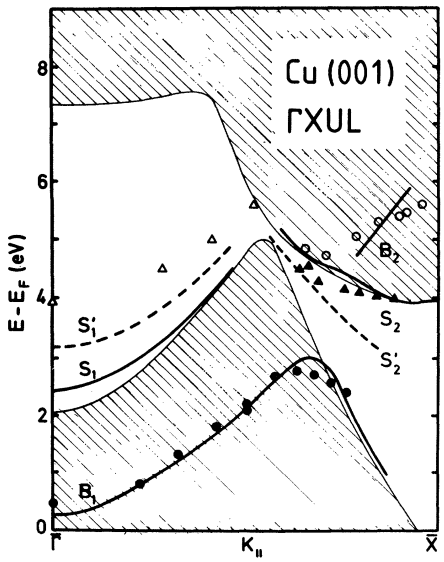

FIG. 2. Bulk band structure of Cu, projected onto the $\bar{\Gamma}$–$\bar{X}$ direction of the surface Brillouin zone. Solid dots and open circles denote experimentally observed bulk direct transitions. Triangles show experimental results on surface-state emission. The heavy lines are results from a theoretical calculation employing the one-step model of inverse photoemission. Dashed curves are for a different choice of the surface-potential barrier.

the attenuation of the clean sample spectra upon oxygen adsorption is indicated by the shaded areas in Fig. 1. Exposition to 5 L of oxygen results in a very small oxygen coverage since it is known and was checked in this work that a c 2×2 overlayer corresponding to half a monolayer requires exposures of the order of 1000 L. In spite of the small coverage obtained at 5 L the surface emission seems to be totally quenched. However, the adsorption test is not unique since a noticeable attenuation of the low-energy bulk direct transition occurs also. A difference spectrum clean minus oxygen exposed for the surface emission region is shown in the inset in the lower right corner of Fig. 1. The full curve in the inset represents the previously measured resolution function. From the good agreement we conclude that the energetic width of the surface state is much smaller than the experimental resolution, as expected.[5] A surface state of similar nature as observed in this work (solid triangles in Fig. 2) is known to exist on Ag(100) from electroreflectance measurements and theoretical calculations.[13]

A further experimental identification of the surface nature of the emission observed in this work would be quite difficult. In general, the independence of the energetic position upon variation of $k_\perp$, the momentum of the electron normal to the surface is taken as a crucial test. However, in the case of surface states penetrating somewhat into the bulk as in the case of surface resonances, an approximate $k_\perp$ conservation can hold and would render such a test useless.[1]

In order to arrive at a more conclusive interpretation in such a complicated situation, we calculated theoretical inverse photoemission spectra for the ΓXUL azimuth of Cu(001). The theoretical energy versus momentum dispersions obtained from these calculations are displayed as heavy solid and dashed lines in Fig. 2. The computational procedure has been described in detail elsewhere.[14] An absorptive part of the potential of $V_i = -0.05$ eV was used in this work, and calculations were performed for various positions of the surface-potential barrier. Volume bands B_1 and B_2 remained entirely unchanged upon such variations. By contrast, the surface emissions denoted by S_1 and S_2 were found to respond quite sensitively to any change of the position of the surface-potential barrier. A good fit to the energetic position and dispersion of the experimentally observed Tamm state S_2 was obtained for the surface barrier at $d = 0.55$ interlayer distances outside the outermost atomic layer. The Tamm state then exists as a resonance within the region of the bulk energy bands and hybridizes with bulk states of the same (positive) parity with respect to the ΓXUL mirror plane. Increasing d from 0.55 to 0.8 interlayer distances shifts S_2 out of the bulk bands to S_2' which now exhibits nearly parabolic dispersion.

Contrary to the Tamm state S_2, the energetic position of the Shockley state S_1 is not satisfactorily reproduced by our calculation. A proper representation of this emission would require much smaller distances of the surface-potential barrier. A trial calculation for $d = 0.45$ is shown as the dashed line in Fig. 2. At $d = 0.45$, however, S_2 moves even deeper into the bulk band region and shows an intensity near the detection limit.

It is, of course, not surprising that energetic position and dispersion of S_1 and S_2 cannot be reproduced by variation of the width of a simple rectangular surface-potential barrier. Such a potential cannot, by whatever choice of its parameters, represent the shape of the long-range image potential. We conclude that by joint efforts of theory and experiment the Shockley and Tamm surface states at Cu(001) provide an opportunity to determine a surface-potential barrier considerably refined compared with the simple but so far exclusively used square-well potential.

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