



Electronic surface band structure of Cu(111) by the 2D Green's function (KKR) method

M. N. Read

School of Physics, University of New South Wales, Sydney NSW 2052, Australia.

Previous surface band calculations for Cu(111) have not produced all experimentally determined surface states for $\bar{\Gamma}$ to \bar{M} . Our present method produces all three states below the Fermi energy and the two between it and the vacuum level. States below the Fermi energy are qualitatively in the correct positions with respect to bulk bands. Further improvements can be made using a more accurate bulk-band potential and selvedge-layer potential.

1. Introduction

In Very Low Energy Electron Diffraction (VLEED) and other spectroscopies, features occur which have been difficult to explain but are thought to be due to a different potential at the top layer of atoms (selvedge layer) from that for atom layers in the bulk (substrate layers).

Features in the surface band structure below the vacuum level would show greatest sensitivity to surface potentials. We wish to use the 2D layer-by-layer Green's function or KKR scattering method to calculate the surface band structure below the vacuum level. This method has not been used previously.

As well as explaining surface band features below the vacuum level in terms of a scattering picture, information obtained concerning surface potentials could then be carried over to the above-vacuum energy range that is probed in VLEED.

2. Method

The layer KKR method uses a scattering picture with a muffin-tin crystal potential to map the 2D bulk band states and surface energy states/resonances. Further details are in Ref. 1. Within each atomic layer the wave function is expanded into spherical waves. Between layers where the potentials are constant, the wave function is expanded into plane waves. The scattering properties of a semi-infinite number of layers can then be combined to represent the crystal. The essential features are that each layer of scattering potential may be different and a semi-infinite number of layers are used.

When the phase change of plane waves on scattering at the surface barrier and bulk substrate is such that a standing wave can form between these regions then a long-lived energy state or resonance exists at the surface. This mechanism produces a Shockley or Rydberg surface state or resonance. A standing wave may also form between the selvedge and substrate layers. This produces a Tamm-type surface state or resonance.

3. Results

Our calculated surface band structure is shown in Fig. 1.

At $\bar{\Gamma}$ near the Fermi level E_f at 8.09 eV, and above, we produce a Shockley surface state at 0.4 eV below E_f (labelled S_0) and a Rydberg surface state at 0.822 eV below E_v (labelled S_1). S_1 is the first Rydberg state arising from scattering at the image tail of the surface barrier potential. These two surface states arise from the penetration of the 00 propagating plane wave into the vacuum region and scattering ~ 5 eV from the top of the surface barrier. Both S_0 and S_1 exactly coincide with the experimental value^{2,3} using our surface barrier model and bulk Cu potential.⁴

At $\bar{\Gamma}$ below E_f , an s-d hybridised bulk band gap is produced centred near 4.2 eV



below E_f . A surface state is located in this gap at 4.5 eV below E_f and coincident with the lower continuum band edge. Two other surface resonances appear above this gap and 2.45 eV and 1.25 eV below E_f . All three of these surface states/resonances arise, in this scattering picture from interaction of the 00 propagating wave and six *evanescent* plane waves, which are the two sets of degenerate plane waves $(01, \bar{1}0, 1\bar{1})$ and $(10, 0\bar{1}, \bar{1}1)$. These evanescent plane waves are attenuated in real space and do not penetrate far into the bulk. The bulk termination allows for their penetration into the vacuum region to produce Shockley-type surface bands in the present model. However they are more localised at the surface than the S_0 surface state.

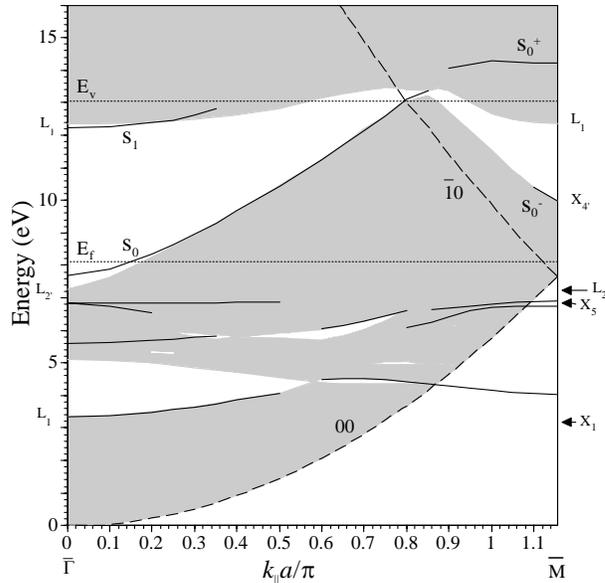


Fig. 1. Plot of the calculation of 2D band structure for Cu(111) surface from $\bar{\Gamma}$ to \bar{M} using the Moruzzi et al Cu potential⁴ and bulk termination with a surface barrier at image-plane position $z_0 = -2.2$ a.u. and cubic polynomial saturation³. Unshaded regions indicate surface-projected bulk-band gaps from this calculation. Full lines are the energies of surface bands from this calculation. E_f is the Fermi level and E_v is the vacuum level. Other symbols on the energy axis indicate various relevant bulk bands and their energy positions as given in Ref. 4. The dashed lines show the energies at which the indicated plane waves become propagating in the crystal surface for different parallel wave vectors, $k_{||}$. The lattice constant is a .

Experimentally a surface state has been detected at 5.25 ± 0.03 eV below E_f at $\bar{\Gamma}$ and coincident with the lower edge of the s-d gap using high-resolution ARPES (angle-resolved photoemission spectroscopy)⁵.

A calculation for Pd(111) surface using a mixed-basis pseudopotential method⁶ and a more recent calculation using a nonlocal density-functional calculation⁷ also produce a surface state in the s-d gap at $\bar{\Gamma}$ and two resonances at high energies in the bulk band continuum. There are only two comprehensive band calculations for Cu(111)^{8,9} and neither have produced the d-like surface state in the s-d gap at $\bar{\Gamma}$. It has been suggested¹⁰ that this is because they are finite slab calculations, and because of its proximity to the bulk band edge, it cannot be distinguished in these cases. S_0 is predicted in Ref. 9 only.

At \bar{M} above E_f , we produce two Shockley surface bands S_0^- , near 2 eV above E_f and S_0^+ , near 6.1 eV above E_f . These bands arise from interaction of the propagating 00 and $\bar{1}0$ plane waves scattering at the mid-point energy of the surface barrier. These waves become propagating at 7.6 eV. The S_0^- band energy agrees with experiment from inverse photoemission^{2,3} for our surface barrier model and bulk Cu potential.⁴ S_0^+ has not been identified from experiment as yet and has not been previously predicted from theory.

At \bar{M} below E_f , the energy location of the d-band continuum is not directly produced in our calculation due to it involving evanescent waves that do not satisfy flux conservation. Inspection of the bulk calculation⁴ puts the edges at $X_5 = 6.77$ and $X_1 = 3.13$ eV with a band gap between X_5 and L_2 at 7.25 eV. We produce a surface state at 6.91 eV in the small s-p band gap and 0.14 eV above the d-band continuum and dispersing downwards towards $\bar{\Gamma}$. Two surface resonances at 4.03 and 6.74 eV are within the d-band continuum. All of these



surface bands arise from interaction of eight evanescent plane waves. Again these evanescent waves leak into the vacuum region to produce very localised surface bands of the Shockley type in the present model.

Experimentally a surface state has been detected at ~ 1.95 eV below E_f at \bar{M} , ~ 0.2 eV above the d-band continuum and dispersing downward towards $\bar{\Gamma}$.^{11,12}

The two calculations for Pd(111)^{6,7} do not reproduce the experimentally determined surface state at \bar{M} about 1 eV below E_f . Of the two other comprehensive calculations of surface band structure for Cu(111)^{8,9}, one⁸ produces the surface state at \bar{M} at 0.3 eV above the d-band continuum and neither produces the S_0^- state.

4. Conclusion

We have been able to reproduce all three surface states of Cu(111) below the Fermi energy that have been found experimentally^{5, 11, 12} and those above it^{2, 3}. The other two previous comprehensive calculations^{8, 9} have not produced all these surface states.

Two of the surface states that are highly localised at the surface are only produced in our calculation from the inclusion of evanescent plane waves.

Our surface states below the Fermi level are qualitatively in the correct position with respect to bulk bands but are not at the correct absolute energies.

One reason is that the Moruzzi potential places the bulk d-band manifold at 0.6 eV higher than the experimental determination.⁴ In particular the position of the X_5 bulk d-band is critical for determining the position of the surface state at \bar{M} below E_f . We find that the bulk band calculation of Burdick¹³ places the X_5 d-band in agreement with experiment¹⁴. Thus we intend to repeat the calculation with this Cu bulk potential.

Another reason for quantitative difference with experiment is that we have abruptly terminated the bulk potential whereas one would expect the top layer to be different. This layer is expected to have approximately 10% d-band narrowing (due to reduced atomic coordination) and d-band shifts of 0.4 to 0.6 eV with respect to bulk bands.^{15, 8} We intend to incorporate this self-edge potential into further calculations.

The fact that the method used here reproduces all the experimentally identified surface states at least qualitatively demonstrates that the method has use in studying the formation of surface bands and details of the surface potentials.

References

1. M.N. Read and A.S. Christopoulos, *Phys Rev B* **45**, 13729 (1992).
2. N.V. Smith, C.T. Chen and M. Weinert, *Phys Rev B* **40**, 7565 (1989).
3. M. Grass, J. Braun, G. Borstel, R. Schneider, H. Durr, Th. Fauster and V. Dose, *J. Phys.: Condens. Matter* **5**, 599 (1993).
4. V.L. Moruzzi, J.F. Janak and A.R. Williams, *Calculated Electronic Properties of Metals*, (Pergamon Press, New York, 1978) p 96.
5. S.G. Louie, P. Thiry, R. Pinchaux, Y. Petroff, D. Chandesris and J. Lecante, *Phys Rev Lett.* **44**, 1782 (1980).
6. S.G. Louie, *Phys Rev Lett.* **40**, 1525 (1978).
7. M. Heinrichsmeier, A. Fleszar, W. Hanke and A.G. Eguiluz, *Phys Rev B* **57**, 14974 (1998).
8. A. Euceda, D.M. Bylander and L. Kleinman *Phys Rev B* **27**, 659 (1983).
9. D.G. Dempsey and L. Kleinman, *Phys Rev B* **16**, 5356 (1977).
10. S.D. Kevan, N.G. Stoffel and N.V. Smith, *Phys Rev B* **31**, 3348 (1985).
11. P. Heimann, J. Hermanson and H. Miosaga, *Phys Rev B* **20**, 3059 (1979).
12. R. Matzdorf and A. Goldmann, *Surf. Science* **359**, 77 (1996).
13. G.A. Burdick, *Phys Rev* **129**, 138 (1963).
14. R. Courths and S. Hufner, *Physics Reports* **112**, 53 (1984).
15. J.A. Appelbaum and D.R. Hamann, *Solid State Commun.* **27**, 881 (1978).