Absence of Surface States in Cu

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The linear combination of muffin-tin orbitals technique has been used to calculate the electronic energy levels of a five-layer Cu (001) film. We do not find any surface states in the s-d gap as had been predicted and calculated in other theoretical studies. Instead we find the energy levels to be nearly indistinguishable from those of the bulk crystal, which agrees with ion-neutralization-spectroscopy data on Cu crystals and with photoemission data from thin overlayers of Cu on Ag substrates.

The linear combination of muffin-tin orbitals (LCMTO) method[1] has been used to calculate the electronic states of a five-layer-thick Cu (001) film. We find that the energy levels correspond closely to those of bulk Cu and that there are no surface states even though the surface-charge regions are included. The absence of surface states for Cu is in agreement with the experimental photoemission data of Eastman and Cashion[2] and with the ion-neutralization-spectroscopy (INS) data of Hagstrum.[3] More recently, Eastman and Grobman[4] have found that photoemission from thin overlayers of Cu on Ag substrates is characteristic of the bulk for overlayer thicknesses greater than four layers. Therefore, our results for a five-layer thin film should be representative of thick films and crystal surfaces.

Absence of surface states in the s-d gap is contrary to previous theoretical predictions[5] and calculations.[6] We are able to find states in the s-d gap when we mix bulk and thin-film states. However, we will show that these states are an artifact resulting from the interface between the thin film and bulk and that these gap states would have been mistaken for surface states if we had limited the film thickness to one or two layers.

Application of the LCMTO method to thin films proceeds exactly as in solids except that the layer structure constants of Kambe[7] are used in place of the bulk structure constants of Ham and Segall.[8]

The Cu (001) thin-film model consists of a total of seven layers. The inner five layers contain Cu atoms with the outermost two layers being empty of Cu atoms. Potentials for the seven layers were constructed by overlapping Herman-Skillman[9] atomic charge densities. The potential in the outer two layers will be referred to as surface charge because it results from the charge-density tails of the five inner layers. Potentials for the outer two occupied layers will be called surface potentials while the potentials for the innermost three layers (which were nearly identical) will be called bulk potentials. Nonspherical corrections to the potential were included since the site symmetry is C_{3v}.

The basis set for layers one to five consisted of thirteen muffin-tin orbitals (MTO) centered on each Cu site and all orthogonalized to the $1s2s2p$ core states. Four MTO's represent the $3s$, $3p$ core states and nine MTO's represent the valence bands. Four MTO's were used for each surface-charge region. At a general k point, our matrix size is 73×73.

The reliability and adequacy of the basis set described above was tested by using this basis set along with the Cu Chodorow potential[10] to calculate the bulk energy bands with our crystal LCMTO energy-band procedure. We find differences of at most 0.005 Ry with the Burdick augmented-plane-wave[11] (APW) values at the Γ, X, and L symmetry points.

The accuracy of our method of constructing potentials was verified by recalculating the bulk energy bands at Γ, X, and L, using the potentials of the innermost three layers. We find, at most, 0.01-Ry differences with the Burdick APW results, thus indicating we have constructed a good potential and basis set.

In Fig. 1(a) the energy states for the seven-layer film at the Γ point of the two-dimensional Brillouin zone are arranged at $\frac{1}{5}$ intervals to emphasize their similarity with the bulk energy bands in Fig. 1(b). Investigation of the thin-film wave functions reveals approximate Bloch symmetry in that the sign of the coefficients of the MTO's alternate as $e^{i\vec{k}\cdot\vec{R}n}$ from layer to layer although the magnitudes of the coefficients from layer to layer are not equal as required for Bloch symmetry. This approximate Bloch symmetry serves

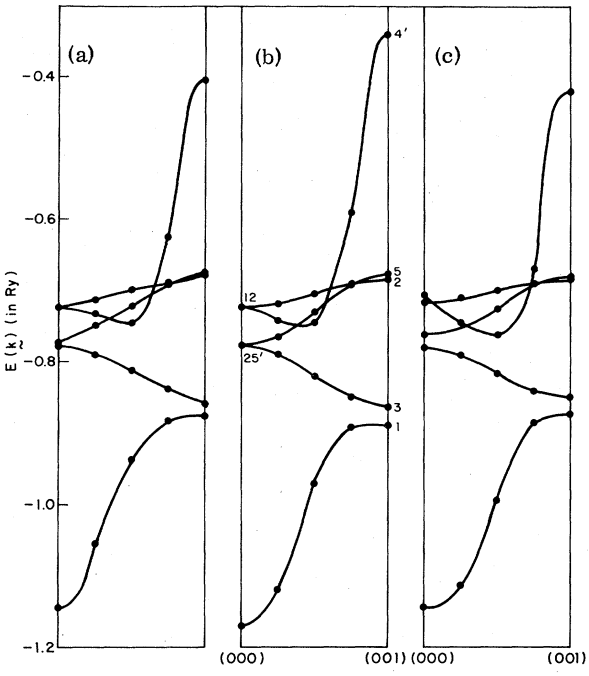

FIG. 1. Comparison of the eigenstates of (a) 5-layer Cu thin film with the eigenstates of (b) 100 layers and (c) 5-layer thick films, respectively, where the wave functions are constrained to Bloch form in (b) and (c).

as further justification for arranging the thin-film energy states to correspond to bulk energy states. Furthermore, the wave functions are found to extend over the full five layers so that none of the states can be interpreted as a surface state.

If the thin-film calculation is repeated without surface charge (the potential is discontinuous at surface), the top of the s-d band which corresponds to $X_{4'}$ is raised from -0.403 to -0.310 Ry, and the state corresponding to X_1 is bent downwards by 0.003 Ry. Surface charge makes quantitative not qualitative differences. Furthermore, the similarity between bulk and thin-film states holds for the Chodorow potential also.

In Figs. 1(b) and 1(c), we graph the results of calculations on 100-layer and five-layer films, respectively, where the wave functions are constrained to Bloch form in the z direction and the surface-charge regions are excluded.

In Table I, we tabulate the band extrema of Fig. 1 and compare to bulk. The 100-layer Bloch-function results are within about 0.02 Ry of the results of a bulk calculation. Thus, we can consider Fig. 1(b) to be representative of the bulk. It is also clear from Fig. 1 and Table I that the

TABLE I. Comparison of thin-film and band states at the Γ point of the two-dimensional Brillouin zone.

Symmetry	Note a	Note b	Note c	Note d
$\Gamma_{25'}$ xz, yz	-0.772	-0.776	-0.762	-0.778
$\Gamma_{25'}$ xy	-0.777	-0.777	-0.780	-0.778
Γ_{12} x^2y^2	-0.721	-0.724	-0.716	-0.720
Γ_{12} s, z^2	-0.725	-0.725	-0.731	-0.720
Γ_1 s, z^2	-1.140	-1.168	-1.145	-1.177
X_5	-0.676	-0.673	-0.678	-0.670
X_3	-0.857	-0.864	-0.850	-0.868
X_2	-0.679	-0.686	-0.685	-0.683
$X_{4'}$	-0.403	-0.339	-0.417	-0.365
X_1	-0.866	-0.889	-0.874	-0.893

[a]Thin-film results of Fig. 1(a).
[b]100-layer results of Fig. 1(b).
[c]5-layer results of Fig. 1(c).
[d]Bulk calculation using potential of innermost layers.

energy states of the thin film in Fig. 1(a) more closely resemble the bulk states than do the five-layer Bloch-function results of Fig. 1(c). For example, the $\Gamma_{25'}$ states are nondegenerate by 0.018 Ry (0.762–0.780) in Fig. 1(c) whereas the nondegeneracy is only 0.005 Ry (0.772–0.777) in Fig. 1(a). Thus, relaxation of the Bloch condition allows the states to assume energy eigenvalues which more closely resemble the bulk values.

In Table II we give the extrema of the thin-film bands as a function of layer thickness in order to show how rapidly the bandwidths approach the bulk values. The table leads one to expect closer correspondence with the bulk if we were to increase the number of layers. For example, the nondegeneracy of the $\Gamma_{25'}$-like states is 0.02 Ry (0.779–0.759) for three layers, 0.012 Ry (0.766–0.778) for four layers, and only 0.005 Ry (0.772–0.777) for five layers.

Comparison of thin-film states and bulk states have also been performed for the X (100) and M ($\frac{1}{2}\frac{1}{2}0$) symmetry points. No surface states appear and the difference between bulk and five-layer thin films is a little larger than at the Γ point but always less than 0.04 Ry.

Previously, surface states had been predicted and calculated in the s-d gap[5,6] between -0.75 and -0.88 Ry. These methods depend upon continuing the bulk wave functions into the surface regions with the matching plane between bulk and surface being one layer or so below the surface.

We now show how states can be introduced into the s-d gap which, however, are not true surface states. The Cu crystal is divided into a 100-lay-

TABLE II. Band extrema at the Γ point of the two-dimensional Brillouin zone as a function of number of layers.

Symmetry	Number of layers 1	2	3	4	5
xz, yz	−0.701	−0.686	−0.680	−0.678	−0.676
		−0.742	−0.759	−0.766	−0.772
xy	−0.793	−0.782	−0.779	−0.778	−0.777
		−0.832	−0.847	−0.853	−0.857
x^2-y^2	−0.682	−0.679	−0.679	−0.679	−0.679
		−0.708	−0.716	−0.719	−0.721
s, z^2	−0.709	−0.571	−0.482	−0.433	−0.403
		−0.734	−0.722	−0.727	−0.725
s, z^2	−0.851	−0.853	−0.866	−0.806	−0.866
		−1.033	−1.098	−1.126	−1.140

er-thick region and a thin-film region of thicknesses between one and five layers. The film is represented by the usual MTO's while the bulk region is represented by the five 100-layer Bloch functions of Fig. 1(b) with $\vec{k}$ vectors (0, 0, 0), (0, 0, 0.2), (0, 0, 0.4), (0, 0, 0.8), and (0, 0, 1). Regardless of film thickness, one state always results in the s-d gap with energy depending on layer thickness but varying between −0.79 and −0.81 Ry. The remaining energy states correspond to those of the bulk states exactly as in the thin-film results of Fig. 1(a). The charge density of the gap state is almost exclusively localized at the layer dividing the thin film from the bulk 100 layers. This gap state can easily be mistaken to be a surface state when a thin-film thickness of one or two layers is used. However, if the thin-film thickness is increased to five layers, this state resides totally within the crystal at the interface region and appears to separate two crystals of Cu. We would expect this gap state to disappear if we include all the Bloch functions of the 100-layer film.

In conclusion, we find no evidence of surface states in Cu. More generally, our results indicate that the relaxation of the Bloch condition on the wave functions may exist deeper into the crystal than the one or two layers now assumed in matching techniques. Relaxation of the Bloch condition near the surface is essential to maintaining close correspondence with bulk states.

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