

Electronic Structure of an Ordered Monolayer of Cu on Zn(0001)

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We have measured the energy distribution curves of photoelectrons ($h\nu = 21.2$ eV) from a Zn single-crystal (0001) face covered by an ordered Cu monolayer and from bulk Cu. We have found a narrow (2.3-eV total width) Cu d -state peak 1.20 eV below the position of the peak of bulk Cu $3d$ structure. We have also calculated the density of states for both a Cu monolayer on Zn and an unsupported Cu monolayer. Theory is in good agreement with experiments. The overlayer density of states is shown to be very similar to that of the unsupported atomic layer.

The study of the electronic structure of very thin metal layers is receiving increasing attention particularly in noble and transition metals where the position and the shape of the d bands are very sensitive to the change from bulk to thin layers. A typical case is that of Cu. The density of states (DOS) of ultrathin Cu layers (one or a few monolayers) has been calculated with various theoretical methods by different authors¹⁻⁴ but even a qualitative agreement among their results is lacking. On the other hand, the situation cannot be clarified by comparing these results with the available experimental data.⁵⁻⁷ The experimental investigation on the DOS of very thin layers can be carried out with photoemission and necessarily concerns layers deposited onto a substrate. An experiment of this kind is fully significant and timely, provided that (i) the atoms in the overlayer are arranged regularly in a known way so that a comparison with theoretical results can be done without ambiguities; (ii) the interaction between the overlayer and the substrate is not excessively strong so that the results can enlighten the physics of the monolayer.

None of the available experimental results satisfies the above-mentioned conditions. In the pioneering work by Eastman and Grobman⁵ the morphology of the Cu overlayer and of the Ag substrate were not characterized, so that the disagreement between their results and recent theoretical works^{4,8} may be nonsignificant.⁹ Abbati and Braicovich⁶ presented results on copper over a zinc polycrystalline substrate deposited by evaporation: This work also does not satisfy condition (i). On the other hand, Heimann, Ned-

dermeyer, and Roloff⁷ used single crystal Ni as a substrate but the interaction of the adsorbate with the substrate is relevant due to the (d - d) interactions between Cu and Ni.

It thus seemed timely to perform an experiment satisfying the above-mentioned conditions and to theoretically study a model which realistically describes the experiment. The results presented here allow substantial progress in the understanding of the problem.

We measured the photoelectron energy distribution curve (EDC) integrated over the angles, excited by He I (21.2 eV) resonance light, from a system consisting on a Cu monolayer evaporated onto a Zn(0001) face freshly cleaved *in situ* (pressure $\approx 1 \times 10^{-10}$ Torr = 1.3×10^{-8} Pa). The deposition was controlled with a quartz oscillator and coverage is accurate within $\pm 15\%$. The morphology was studied *in situ* by low-energy electron diffraction: The Cu atoms form an ordered overlayer having the same geometry as a plane of the hcp crystal. Thus the deposited monolayer has the same periodic arrangement as a (111) atomic plane of a fcc Cu crystal, with a small increase (4%) of the intra-atomic distance. We did not try to measure the distance between the overlayer and the first plane of the substrate, nor to establish if the Cu atoms occupy the positions that continue the hcp sequence or if a stacking fault occurs. This information is not critical in the interpretation of the experiment as it will be shown later.

The Cu-Zn system also satisfies condition (ii) since the effect of the (d - d) interaction between Cu and Zn is small, because of the distance in energy between the two d bands. Problems could

arise from the fact that Cu tends to diffuse into Zn; we extensively studied this process in a separate experiment.¹⁰ In the present measurements taken immediately after evaporation this process has negligible influence.

The EDC taken on the system consisting of the ordered Cu overlayer on the Zn(0001) face is given in Fig. 1(a); the $3d$ Zn peak is located 9.9 eV below E_F and Cu $3d$ electrons appear as an asymmetric line with a maximum located at 3.70 eV below E_F and having a total width of about 2.3 eV (defined by extrapolation of the edges). The center of gravity is at 3.77 eV. For the sake of comparison we give in Fig. 1(b) the results of Ref. 6 for approximately the same number of Cu atoms per unit area onto an evaporated Zn substrate. The differences between the two cases are dramatic; in case (b) the maximum is located

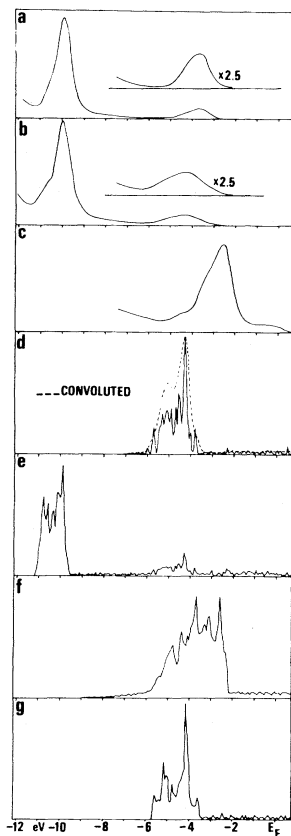


FIG. 1. Energy distribution curves for (a) one Cu ordered monolayer on Zn(0001) face, (b) about one monolayer of Cu on a polycrystalline Zn film, and (c) thick Cu layer. Theoretical results are given for (d) the local density of states of a Cu overlayer and the total density of states of (e) Cu and Zn, (f) bulk Cu, and (g) the isolated monolayer.

4.25 eV below E_F , the line has a total width of about 3.3 eV and is more symmetric. The difference in location may be understood if one considers that, in case (b), grain boundary diffusion of Cu causes a phase in which Cu is more dilute so that the d peak is shifted to higher binding energies.^{10,11} The considerable linewidth strongly suggests that contributions from Cu in different sites are present. The comparison between these results and the EDC of bulk Cu constitutes the phenomenological basis of the discussion presented below. The EDC of bulk Cu was taken after the evaporation of thirty times the Cu quantity of case (a). It appears clearly that, in the overlayer case, the maximum of the $3d$ structure is shifted 1.20 eV with respect to the maximum of the corresponding bulk structure while a considerable narrowing of it is seen; the center of gravity shift is 1 eV and that of the upper edge is 1.15 eV.

In what follows we compare the measured EDCs with calculated DOS (which neglect the effects of matrix elements and final states as it is commonly done) in order to discuss the relevant features of the occupied electron states. The DOS was calculated using a tight-binding approach. The system is described as a regular stack of thirteen atomic planes of Zn plus one plane of Cu on each side of the slab. Taking an $sp-d$ basis set per atom, the one electron Hamiltonian of the layer was described through the Slater-Koster parametrization scheme,¹² a method which has given good results in the study of surface states both for transition metals¹³ and semiconductors.¹⁴ The values of the parameters within the two-center approximation and including hopping integrals up to second neighbors for Zn and up to third neighbors for Cu were obtained from a fit to the bulk electronic structure (Segall¹⁵ for Zn and Burdick¹⁶ for Cu). For Cu hopping integrals an interpolation is also required since the interatomic distances of the adsorbed monolayer are slightly different from the bulk ones. The interaction integrals between Zn and Cu can be estimated reliably by assuming them to be the average of the corresponding (and rather close) values of Zn-Zn and Cu-Cu hopping integrals, evaluated at the appropriate distance.

To achieve self-consistency we use the method described in Ref. 4 since the intra-atomic parameters (ss)₀, (pp)₀, and (dd)₀ are allowed to vary at each atomic plane with the excess charge and electron configuration in the same way as the valence-orbital ionization potential of the free

atoms.¹⁷ Self-consistency is important in determining the electronic orbital configuration at the surface and the position of the d peak of the overlayer with respect to E_F .

The calculated local density of states of the overlayer is given in Fig. 1(d); the result of the convolution with a broadening function (300 meV wide) is also given to account for the resolution and the electron scattering effects. The d resonance extends from 3.75 to 5.7 eV below E_F with a center of gravity at 4.71 eV and a maximum at 4.26 eV. The total DOS of the fifteen planes is given by Fig. 1(e) where the d -band structures of Zn and Cu are clearly seen. The DOS calculated for Cu crystal is shown in Fig. 1(f): The d structure is much wider and extends from 2.2 to 5.6 eV with the center of gravity at 3.58 eV. The agreement between theory and experiment is satisfactory since in both cases a shift of the d structure towards higher binding energies and a narrowing of the peak is found. The shift of the upper edge of the calculated structure is 1.55 eV while that of the center of gravity is 1.13 eV. The measured shift is somewhat smaller; this could be due, at least in part, to the fact that the electron relaxation contribution in the measured spectra is probably higher in the Cu overlayer than in the bulk, due to the higher localization of d electrons. Also the comparison of the line shapes is encouraging, although a detailed analysis is beyond the scope of the present discussion.

The narrowing of the d band is due to the decrease of the number of nearest neighbors in the overlayer with respect to the bulk (from 12 to 6 Cu atoms). The new atomic arrangement of the overlayer is also responsible for the location of the d peak with respect to E_F : The average density of states in the lower part of the conduction band is decreased so that the distances between E_F and the d structure is increased; the d occupancy becomes larger so that copper is more atomic in the overlayer.¹⁸

This description is in agreement with the one provided by the normalized atom approach,¹⁹ where the shift of the d band towards higher binding energies may be seen as a consequence of the sp charge decompression at the surface with respect to the bulk.

The calculated shift is the result of the new environment of the Cu atoms and of an opposite but a smaller shift (0.3 eV) due to the change in configuration accounted for by the iterative procedure. The final d occupancy is 9.963, to be compared with the value 9.886 obtained for bulk

Cu.

It is important to note that this picture is basically the same for the isolated monolayer and for the overlayer, with the obvious difference that in this last case E_F is fixed by equilibrium with the substrate. In fact, a calculation of the DOS of an isolated monolayer, having the same interatomic distances as the overlayer, gives the results of Fig. 1(g), which are qualitatively similar to the results of the local density of states of the overlayer of Fig. 1(d). The d occupancy for the unsupported Cu monolayer is 9.969, thus indicating a more atomic copper with respect to bulk also in this case. This shows that the greatest part of the measured features are also typical of the isolated monolayer.

The reliability of our theoretical results are moreover supported by the following considerations: (i) The results depend very slightly on the different description of the bulk bands. Another calculation was performed with the Cu parameters obtained through a fit to the band structure given by Smith and Mattheis²⁰ which differs from Burdick's¹⁶ basically in the treatment of the exchange and correlation potential: The results are negligibly influenced. We also found that no change is obtained in the local density of states of the overlayer by shifting the position of the bulk Zn d bands by ± 2 eV. This is important since the location of Zn d band is controversial.²¹ (ii) The choice of the distance between the overlayer and the substrate is not critical: A calculation with 12% lower distance gives no appreciable differences in the d -state location and structure. (iii) We ascertained that the presence of a fault in the stacking sequence of the overlayer with respect to the substrate has a negligible influence on the DOS.

In conclusion we have found a narrowing and a shift of Cu d state of the monolayer with respect to the bulk. We have shown that these effects are accompanied by a change of the atomic configuration which becomes intermediate between that of the atom in the bulk crystal and that of the isolated atoms.

This conclusion stands on general arguments connected with the change in the geometry and applies, very probably, to other systems and not only to the copper case treated here. We hope that this result will stimulate further experimental and theoretical work in the field.

¹B. R. Cooper, Phys. Rev. Lett. **30**, 1316 (1973).

²S. J. Gurman, J. Phys. F **5**, L194 (1975).

- ³J. G. Gay, J. R. Smith, and J. F. Arlinghaus, *Phys. Rev. Lett.* **38**, 561 (1977).
- ⁴C. M. Bertoni, O. Bisi, C. Calandra, and F. Manghi, *Thin Solid Films* **43**, 251 (1977).
- ⁵D. E. Eastman and W. R. Grobman, *Phys. Rev. Lett.* **30**, 177 (1973).
- ⁶I. Abbati and L. Braicovich, in *Proceedings of the Seventh International Vacuum Congress and Third International Conference on Solid Surfaces*, Vienna, Austria, 12–16 September 1977, edited by R. Dobrozemsky, F. Rüdener, F. P. Viehböck, and A. Breth (to be published).
- ⁷P. Heimann, H. Neddermeyer and H. F. Roloff, in *Proceedings of the Seventh International Vacuum Congress and Third International Conference on Solid Surfaces*, Vienna, Austria, 12–16 September 1977, edited by R. Dobrozemsky, F. Rüdener, F. P. Viehböck, and A. Breth (to be published).
- ⁸O. Bisi and C. Calandra, *Surf. Sci.* **67**, 416 (1977).
- ⁹Eastman and Grobman (Ref. 5) studied Pb and Cu over Ag; Bisi and Calandra (Ref. 8) compared these results with a calculation for Cu and Pd on (001) face of Ag. For the Cu/Ag system they found a substantial disagreement since they calculated a strong shift of the *d*-state peak towards higher binding energies which is not seen in the experiments.
- ¹⁰I. Abbati, L. Braicovich, and P. Jona, in *Proceedings of the Fifth International Conference on Vacuum Ultraviolet Radiation Physics*, edited by M. C. Castex, M. Poney, and N. Poney (Centre National de la Recherche Scientifique, Montpellier, 1977), Vol. II, p. 204.
- ¹¹P. T. Andrews and L. A. Hiscott, *J. Phys. F* **5**, 1568 (1975).
- ¹²J. C. Slater and C. Koster, *Phys. Rev.* **94**, 1458 (1954).
- ¹³K. S. Sohn, D. G. Dempsey, L. Kleinman, and E. Caruthers, *Phys. Rev. B* **14**, 3185 (1976), and references therein; C. M. Bertoni, C. Calandra, and F. Manghi, *Solid State Commun.* **23**, 255 (1977).
- ¹⁴K. C. Pandey and J. C. Phillips, *Phys. Rev. Lett.* **32**, 1433 (1974); C. Calandra, F. Manghi, and C. M. Bertoni, *J. Phys. C* **10**, 1911 (1977).
- ¹⁵B. Segall, *J. Phys.* **33**, C3-27 (1972); the calculated band structure located the Fermi level at about 6 eV from the vacuum level. We shifted the *s-p* bands upward to get a more realistic work function; in this way the *d* band is located 10.2 eV from E_F , with a better agreement with the results obtained both from ultraviolet photoelectron spectroscopy and x-ray photoemission spectroscopy measurements.
- ¹⁶G. A. Burdick, *Phys. Rev.* **129**, 138 (1963).
- ¹⁷D. W. Bullett and M. L. Cohen, *Solid State Commun.* **21**, 157 (1977).
- ¹⁸An analogous effect has been recently suggested for Pd atoms in small clusters by M. G. Mason, L. J. Gerenser, and S.-T. Lee, *Phys. Rev. Lett.* **39**, 288 (1977).
- ¹⁹L. Hodges, R. E. Watson, and H. Ehrenreich, *Phys. Rev. B* **5**, 3953 (1972).
- ²⁰N. V. Smith and L. F. Mattheiss, *Phys. Rev. B* **9**, 1341 (1974).
- ²¹L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. R. Shirley, *Phys. Rev. B* **8**, 2392 (1973).

Valley-Valley Splitting in Inversion Layers on a High-Index Surface of Silicon

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The superlattice phenomenon observed by Cole, Lakhani, and Stiles in the electron inversion layer on (119)Si is explained by projecting the bulk band structure onto the surface. On high-index surfaces, the valley degeneracy only occurs at the surface-band-structure zone boundary. Lifting this degeneracy gives rise to minigaps which we observe in the optical conductivity as interband absorption.

In a silicon MOSFET (metal-oxide-semiconductor field-effect transistor) with an interface of Si tilted away from the high-symmetry plane (001) to a high-index plane such as (119), Cole, Lakhani, and Stiles¹ have found structures in the dc conductivity and unusual oscillations in the magnetoconductivity. They explained the observed phenomena in terms of a model of a one-dimensional superlattice along the interface. The precise cause of the formation of the superlattice is, however, unknown.

We present an alternative explanation in terms

of valley splitting^{2,3} between the two conduction-band minima in the [001] direction. The formation of an energy gap in the $[\bar{1}\bar{1}n2]$ direction on the tilted (11*n*) Si-SiO₂ interface follows naturally and the so-called "superlattice period" as a function of tilted angle is easily explained. Furthermore, we have measured the optical conductivity and observed a peak due to the interband transitions across the minigap. While the dependence of the energy gap on electron density is consistent with both our valley-splitting model and the superlattice model, the observed intensity of the inter-