



# Electronic properties of a pseudomorphic Cu-layer on Ni(111)

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## Abstract

The band structure of a monolayer Cu on Ni(111) was studied both by angle resolved UV photoemission spectroscopy (ARUPS) and density functional (DF) calculations. The Cu 3d-bands at binding energies between 2 eV and 5 eV show a very pronounced  $k_{\parallel}$  dispersion along the  $[11\bar{2}]$  and  $[\bar{1}10]$  substrate directions, but no dispersion with  $k_{\perp}$ . This proves the two-dimensional character of the Cu 3d-bands. The periodicity of the bands coincides with the periodicity of the Ni(111) surface. The experimentally determined two-dimensional band structure of the pseudomorphic Cu monolayer on Ni(111) is in very good agreement with the results of DF calculations on the system. From this comparison we obtain detailed information about the Cu/Ni interaction and the  $k$ -dependent coupling of Cu and Ni bands. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

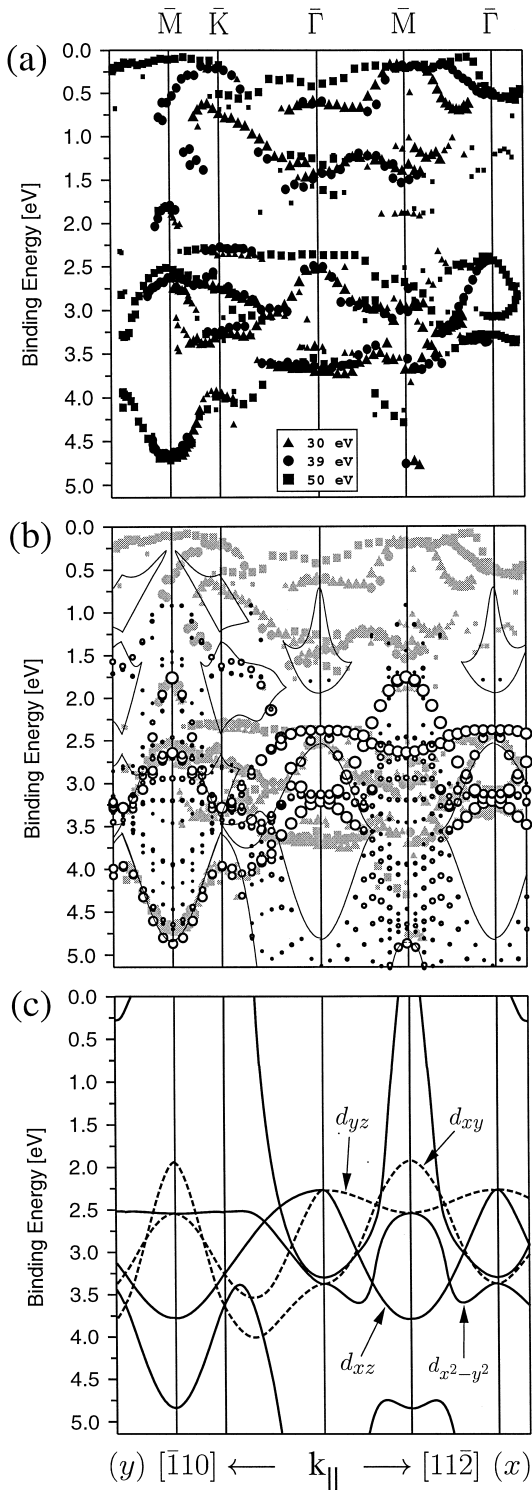
Mixed metal systems have important technological applications in the areas of metallurgy, catalysis, electrochemistry, and microelectronic fabrication. Systematic investigations about the nature of heteronuclear metal–metal bonds are necessary for a general understanding of the physical and chemical properties of various material combinations. In the present study we have investigated ultrathin Cu layers on a Ni(111) surface. Ni and Cu have very

similar geometric structure: both metals are fcc crystals; the lattice mismatch of 2.5% ( $a_{\text{Cu}} = 3.61 \text{ \AA}$  vs.  $a_{\text{Ni}} = 3.52 \text{ \AA}$ ) is relatively small so that one can expect pseudomorphic growth. On the other hand the electronic properties of Ni and Cu are very different: Cu being a coinage metal has a completely filled 3d-shell and therefore no occupied d-states at the Fermi level; Ni being a transition metal has an open 3d-shell and therefore a high density of d-states at the Fermi level. This difference in the electronic structure is responsible for the higher chemical reactivity of Ni as compared to Cu. Despite the fact that Cu/Ni material combinations are difficult to study because the two metals intermix at high tempera-

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by small symbols. The total error bar for energy values (monochromator, analyser, peak determination) is 0.2 eV and  $0.15 \text{ \AA}^{-1}$  for  $k_{\parallel}$ . The Cu dominated bands ( $E_B = 2\text{--}5$  eV) clearly exhibit a two-dimensional band structure as is concluded from the absence of any photon energy dependence within the error margin of the experiment. The periodicity of the Cu bands is in agreement with the surface Brillouin zone of Ni(111), another evidence for the pseudomorphic ( $1 \times 1$ ) structure of the Cu monolayer. While we cannot deduce the site of Cu atoms on Ni(111) by ARUPS, in an DF calculation (see below) we found the fcc stacking order roughly 0.01 eV/Cu more stable than the hcp stacking order.

For a better understanding of the experimental band structure ‘first-principles’ density functional (DF) slab model calculations have been performed. The full-potential linear-augmented plane wave (FLAPW) technology as implemented in the WIEN95 code [11,12] is applied for that purpose. The adsorption system is modelled by a 7 layer Ni substrate with one Cu layer adsorbed at the position of the next Ni layer on both sides of the slab. Because of well-known tendencies in DF one-particle spectra to underestimate valence ionization energies, the calculated band structure was down shifted by 0.4 eV to enhance agreement with the experiment ( $E_{\text{Fermi}} \equiv 0$  eV). In Fig. 2b, the calculated band structure (open circles) is compared to the measurements (grey symbols). As a guidance the projected Ni bulk band structure is shown as well (black lines). The amount of Cu population in each  $k_{\parallel}$ -resolved state is indicated by the circle radius. States with minor (or no) Cu population are not displayed for the sake of clarity. For small binding energies, i.e.,  $E_B < 1.5$  eV, only Ni states are observable, as is confirmed by

Fig. 2. (a)  $E_B(k_{\parallel})$ -dispersion of a pseudomorphic Cu monolayer on Ni(111), measured at  $\hbar\omega = 30$  eV, 39 eV, and 50 eV, along the two high symmetry directions ( $[\bar{1}1\bar{2}]$  and  $[\bar{1}10]$ ). Small symbols represent less dominant peaks. (b) Calculated band structure for a pseudomorphic Cu monolayer on Ni(111) (open circles), plotted together with measured data (grey symbols) and the projected Ni bulk band structure (black lines). The calculated band structure was uniformly shifted to higher binding energies by 0.4 eV (see text). (c) Calculated band structure for an unsupported Cu monolayer (shifted to higher binding energies by 0.8 eV).

the population analysis of the calculated band structure.

The coupling of the Cu derived states to the substrate sensitively depends on the position in  $k$ -space. As evident from Fig. 2b, at the  $\bar{\Gamma}$  and  $\bar{K}$  points most of the calculated Cu bands happen to fall into the large band gaps of the surface-projected bulk band structure of the Ni substrate. This leads to a weak coupling between Cu and Ni states near these high symmetry points in  $k$ -space. This fact is reflected by both our experimental and calculated data: the Cu 3d-bands for one monolayer Cu/Ni(111) show much resemblance to the calculated band structure (Fig. 2c) of an unsupported two-dimensional Cu monolayer, contracted to the lattice constant of Ni. The overall agreement of the experimental data with these calculations is very good. The only exception is a non-dispersing state at  $E_B = 3.75$  eV near  $\bar{\Gamma}$ . We attribute this state to isolated Cu atoms on top of the pseudomorphic Cu monolayer. This interpretation is confirmed by the fact that the same isotropic emission peak is observed for (isolated) Cu atoms in condensed benzene or water layers [13].

Near the  $M$  points there are no band gaps of the projected Ni band structure in the energy range  $E_B = 0$ –5 eV. Profound coupling of Cu and Ni is therefore possible, provided two bands have the same symmetry. This is the case for the Cu  $d_{xz}$  and  $d_{x^2-y^2}$  bands (denotation taken from the unsupported monolayer in Fig. 2c) which are *even* with respect to the mirror plane defined by the surface normal and the  $[11\bar{2}]$  azimuth. Apparently they strongly interact with the bottom of the substrate d-band, i.e., *even* substrate states of mainly  $d_{xz}$  and  $d_{x^2-y^2}$  character. As a consequence, the Cu-induced states in Fig. 2a,b no longer follow the band structure of an unsupported Cu monolayer. Instead, the Cu states at  $E_B = 3.8$  eV and 2.5 eV (at the  $\bar{M}$  point) couple to a large manifold of substrate Bloch states and thus upon interaction turn into a set of eigenstates in the energy range from 2.5 to 4.5 eV with only minor Cu contribution in each of them. This resonance is too broad to be detected as significant photoemission peak(s). It mainly contributes to the background intensity, similar to the Cu 4s-levels. On the other hand, at the  $\bar{M}$  point the Cu  $d_{yz}$  and  $d_{xy}$  states of the unsupported Cu monolayer ( $E_B = 1.9$  eV and 2.5 eV) are *odd* with respect to the mirror plane ( $[11\bar{2}]$

azimuth). Therefore, they cannot interact with the Ni d-states which are *even* in this energy range, and hence the corresponding bands are not significantly altered by the presence of the Ni substrate.

Since our measurements have been performed with polarized synchrotron radiation, symmetry selection rules have to be considered. For all measurements the plane of detection,  $D$ , was parallel to the electric field vector  $\vec{E}$  of the incoming light ( $D \parallel \vec{E}$ ). No symmetry selection rules are applicable for detection along  $[\bar{1}10]$  (i.e.,  $\bar{\Gamma} \bar{K} \bar{M}$ ), because the vertical plane aligned along  $[\bar{1}10]$  ( $\equiv yz$ -plane) is no symmetry plane of an fcc(111) surface. Thus all Cu induced states should be observable in this experimental set-up. A completely different situation is encountered along the  $[11\bar{2}]$  direction (i.e.,  $\bar{\Gamma} \bar{M} \bar{\Gamma}$ ). Now the system is symmetric with respect to the detector plane ( $C_{s,\sigma(xz)}$ -symmetry) and its eigenstates can be subdivided into *even* and *odd* states. Because the polarization of the incoming photon is chosen parallel to the detector plane ( $D \parallel \vec{E}$ ), only *even* states can contribute to the photoemission signal; *odd* states are ‘symmetry forbidden’. In detail, this implies that the *odd*  $d_{xy}$  and  $d_{yz}$  derived Cu states are allowed along  $[\bar{1}10]$  and forbidden along  $[11\bar{2}]$ . All remaining Cu d-bands ( $d_{z^2}$ ,  $d_{xz}$ ,  $d_{x^2-y^2}$ ) are symmetry allowed in both orientations of the detector plane. Our experimental data confirm these predictions. The fact that the  $d_{xy}$  derived state is also observed in the ‘forbidden’  $[11\bar{2}]$  direction – though with small intensity (small symbols), as one can see in the raw data (Fig. 1) – is attributed to the incomplete polarisation ( $\sim 80\%$ ) of the synchrotron radiation.

#### 4. Conclusion

In conclusion, the ARUPS data of a pseudomorphic monolayer Cu/Ni(111) are in good agreement with the two-dimensional band structure obtained from the DF slab model calculations. The amount of coupling between Cu and Ni states is found to depend strongly on the crystal momentum associated with each state. Starting from an unsupported Cu monolayer and taking into account the electronic interaction of the Ni(111) substrate as well as symmetry selection rules, we obtain a detailed understanding of the electronic structure of the Cu–Ni surface.

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