Correlation between chemical properties and electronic structure of pseudomorphic Cu monolayers on Ni(111) and Ru(0001)

H. Koschel a,b, U. Birkenheuer c,1, G. Held a,b, H.-P. Steinrück a,b,*

a Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstrasse 3, D-91058 Erlangen, Germany
b Experimentelle Physik II, Universität Würzburg, D-97074 Würzburg, Germany
c Theoretische Chemie, Technische Universität München, D-85747 Garching, Germany

Received 13 October 2000; accepted for publication 12 January 2001

Abstract

The adsorption of CO and benzene on pseudomorphic Cu monolayers on Ni(111) and Ru(0001) shows pronounced differences: For Cu/Ni(111) a behavior very similar to that of Cu(111) is observed, for Cu/Ru(0001) the adsorbate substrate bond is significantly strengthened for both molecules, as is deduced from a shift of the desorption temperature to higher values. Based on angle resolved UV photoelectron spectroscopy using synchrotron radiation at BESSY and density functional calculations we have determined the two-dimensional band structure of the pseudomorphic Cu monolayers on Ni(111) and Ru(0001). Our results show that for Cu/Ni(111) only weak coupling of the Cu 3d states to the Ni substrate states occurs. On the other hand, strong coupling is observed for Cu/Ru(0001). This difference is made responsible for the strongly modified chemical properties of Cu/Ru(0001) as compared to Cu/Ni(111). © 2001 Published by Elsevier Science B.V.

Keywords: Copper; Nickel; Ruthenium; Metallic films; Carbon monoxide; Chemisorption; Angle resolved photoemission; Density functional calculations

1. Introduction

Bimetallic surfaces have received considerable interest recently [1–40], due to their importance in the fields of catalysis, metallurgy, electrochemistry and microelectronic fabrication. Their electronic, structural, chemical, and catalytic properties have been studied in some detail by a variety of experimental methods. It was shown that upon deposition of one metal onto another new structures can be formed which are not seen in bulk alloys. One particularly interesting class of systems are pseudomorphic monolayers. By choosing different substrates, with different electronic structures and lattice constants, the electronic and geometrical properties of the pseudomorphic monolayers can be changed. As a consequence, the reactivity of the

*Corresponding author. Address: Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstrasse 3, D-91058 Erlangen, Germany. Tel.: +49-9131-85-27343; fax: +49-9131-85-28867.
E-mail address: steinrucek@ptc.chemie.uni-erlangen.de (H.-P. Steinrück).
1 Permanent address: Max-Planck Institute for the Physics of Complex Systems, D-01187 Dresden, Germany.

0039-6028/01/$ see front matter © 2001 Published by Elsevier Science B.V.
PII: S0039-6028(01)00889-5
metal layer towards adsorbate molecules can be significantly modified. Owing to its importance as a model adsorbate in surface science and catalysis, the interaction of CO with such systems has been studied in much detail [2-4,8-11,25-29,33,34,38,39]. It has been shown that significant shifts of the desorption temperature of CO occur for a monolayer of a transition metal (e.g. Pd) or a noble metal (e.g. Cu) on a transition metal surface as compared to the corresponding surface of the pure material. These changes have been correlated with shifts in the surface core level binding energies [2,4,10,11]. In a recent theoretical study Hammer et al. [12] showed that the reactivity of the adlayer is connected with the position of the center of gravity of its d-states. In another study Hennig et al. [13] pointed out that the major reason for the changed reactivity of the metal adlayer is a charge polarization within the adlayer rather than a charge transfer to the underlying substrate.

The aim of the present paper is to contribute to a more detailed understanding of the correlation between electronic and chemical properties of ultrathin metal layers. Following a very recent study of our group on the band structure of Cu/Ni(111) [37] we concentrate here on the comparison of the properties of pseudomorphic Cu monolayers on Ni(111) and Ru(0001). Both substrates are reactive transition metals, whereas the deposited monolayer represents a relatively inert coinage metal. The different substrates have been chosen for several reasons: (1) Pseudomorphic Cu monolayers can be reproducibly prepared with good structural quality on both Ru(0001) [14,15,17,19,20,23,24,38,39] and Ni(111) [30-34,37]. (2) The surface lattice constant of 2.55 Å for a Cu(111) crystal is larger than the value of 2.49 Å for Ni(111) but smaller than the value of 2.71 Å for Ru(0001): therefore, one obtains a compressed (lattice mismatch −2.5%) and a expanded (lattice mismatch +6.0%) pseudomorphic Cu layer on the two surfaces, respectively. (3) The electronic structures of the two substrates (Ni: 3d metal and Ru: 4d metal) are quite different, which should result in significantly different coupling of the electronic states. In order to characterize the chemical properties we compare the adsorption properties of CO and benzene on Cu/Ni(111) and Cu/Ru(0001) with each other and with the behavior on the bare Cu(111), Ni(111) and Ru(0001) surfaces. For a detailed understanding of the electronic structure of the pseudomorphic Cu monolayers on Ni(111) and Ru(0001) we have determined the k-resolved band structure of the two systems by angle resolved UV photoelectron spectroscopy (ARUPS). These experimental results are then compared to quantum mechanical model calculations for an unsupported Cu monolayer at the lattice constant of the two substrates and for density functional (DF) slab model calculations simulating the experimental situation. While there are a few studies addressing the electronic structure of Cu/Ni [30] and Cu/Ru [10,11,17,23,29], to our knowledge, no comparable experimental or theoretical studies of the k-resolved band structure of bimetallic systems are available in the literature.

2. Experimental

The experiments were carried out in a two-chamber ultra high vacuum (UHV) system, consisting of a preparation chamber and an analyzer chamber, both operating at a base pressure below 2×10⁻¹⁰ mbar (for a detailed description see Ref. [41]). It is equipped with a quadrupole mass spectrometer for TPD, low energy electron diffraction (LEED) optics, an ion sputtering gun, a commercial electron bombardment evaporator (Focus EFM3) and a capillary gas doser. The ARUPS measurements were recorded using linearly polarized synchrotron radiation from the TGM-1 monochromator at the German synchrotron facility BESSY-I in Berlin. A homebuilt multichannel electron analyzer [42,43] allows simultaneous detection of electrons emitted under polar angles, $\vartheta$, from −10° to 90° (with respect to the surface normal) at a fixed azimuth angle. The polar angle resolution is better than ±1° at an azimuthal acceptance of $\sim \pm 1.5°$. The combined energy resolution of monochromator and analyzer was better than 200 meV in all cases. Measurements were obtained at photon incident angles of $\alpha = 45°$. The plane of detection, $D_{\alpha}$, was always coplanar with the plane defined by the electric field
vector $\vec{E}$ of the incoming light and the surface normal $\langle D | \vec{E} \rangle$. Angle resolved spectra are integrated over $\pm 1.5^\circ$ of the nominal polar angle $\theta$; angle integrated spectra are integrated from $-10^\circ$ to $90^\circ$. All ARUPS data were recorded at a sample temperature around 80 K.

The Ni(111) and the Ru(0001) crystals were cut by spark erosion from single-crystal rods and oriented by the Laue method with an accuracy better than 0.5°. They were cleaned in UHV using standard procedures [44,45]. Surface order was controlled by LEED; in addition, surface cleanliness of both samples was checked by TPD measurements of adsorbed probe molecules (CO, benzene), which were compared to reference spectra recorded earlier [46–51]. The samples could be cooled down to 80 K by liquid nitrogen cooling, and were resistively heated using linear heating rates.

The pseudomorphic Cu monolayer on Ni(111) was prepared by evaporating the appropriate amount of Cu onto the cold substrate at an evaporation rate of $\sim 0.3$ ML per minute (where 1 ML is defined as one adsortate atom or molecule per substrate surface atom) followed by heating the sample to 700 K with a linear heating rate of 5 K/s, and finally cooling down to 80 K [37]. The Cu coverage was determined by titration of the uncovered Ni areas with CO using TPD and X-ray photoelectron spectroscopy (XPS) [34]. Due to Cu–Ni alloying at temperatures above 800 K [34], Cu had to be removed from the Ni crystal by Ar ion sputtering [33,34,37]. The clean sample was typically restored by sputtering with 1000 eV ions at a current of 8 $\mu$A for 15 min at a temperature of 80 K, and subsequent annealing at 1220 K for 120 s. The pseudomorphic Cu monolayer on Ru(0001) was prepared by depositing Cu onto the substrate at 1067 K and a rate of 0.3 ML per minute. Under these conditions a well defined pseudomorphic Cu monolayer is formed [38–40]. The clean sample was restored by flashing to 1400 K and thereby desorbing the adsorbed Cu atoms. The resulting Cu monolayers on Ni(111) and Ru(0001) both show a very sharp ($1 \times 1$) LEED pattern, indicating a well-ordered pseudomorphic structure.

Benzene and CO were dosed using a glass multicapillary doser, which yields a homogeneous gas flux over the surface at a low background pressure rise in the preparation chamber; thereby post adsorption after the dosing process is minimized [46]. The adsorbate coverages were determined by TPD with an accuracy of $\pm 5\%$. TPD spectra were recorded using a Balzers 211 quadrupole mass spectrometer equipped with a Feulher cup [52], at linear heating rates of 1 or 5 K/s. Deuterated benzene (C$_6$D$_6$) was used in order to minimize the effects of H$_2$ background in TPD.

### 3. Results and discussion

#### 3.1. Temperature programmed desorption of CO and benzene

In order to investigate the chemical properties of the pseudomorphic Cu monolayers on Ni(111) and Ru(0001), we have studied the adsorption of CO and benzene on these two surfaces and compared the spectra to those obtained for the bare substrates and for Cu(111).

The TPD spectra of CO are shown in Fig. 1. For each surface they correspond to saturation coverage or to a coverage close to saturation coverage at adsorption temperatures between 80 and 100 K. For Ni(111) and Ru(0001) desorption is observed mainly in the temperature range between 300 and 500 K, with the shape of the spectra in excellent agreement with the literature [47–50,53]. For Cu(111) desorption occurs between 100 and 185 K (the arrows in the figure indicate the temperature, where desorption is completed); again the spectrum is in good agreement with the literature [39,54–58]. For Cu/Ni(111) and Cu/Ru(0001) significant changes in the shape of the spectra, but also in the temperature range, are observed that depend on the underlying substrate: For Cu/Ni(111) the desorption is terminated at 200 K, i.e. 15 $\pm 5$ K above the value observed for Cu(111) [59]. CO on Cu/Ru(0001) displays a much larger shift of 70 $\pm 5$ K. The shift observed for Cu/Ru(0001) is in very good agreement with values reported in the literature [25–29,38,39], for Cu/Ni(111) no information is available.

In Fig. 2 the TPD spectra after benzene adsorption on the various surfaces are shown. After
dosing benzene at low temperatures the sample was heated to 900 K at a constant heating rate of 5 K/s. Simultaneously, the partial pressures of $C_8D_6$ ($m/e = 84$) and $D_2$ ($m/e = 4$) were recorded. For Ni(111) and Ru(0001), the adsorbed benzene layers corresponded to well ordered ($\sqrt{7} \times \sqrt{7}$)R19.1° structures with a coverage of 0.14 ML. For both surfaces the desorption spectra of $D_2$ and $C_8D_6$ perfectly reproduce the behavior reported in the literature [46,51]. For Ni(111), molecular benzene desorption is observed between 275 and 460 K. In addition, desorption of $D_2$ occurs between 400 and 700 K, indicative of benzene decomposition upon heating. The quantitative analysis of TPD areas yielded a fraction of 40% of dissociated benzene molecules [46], which demonstrates the high reactivity of the Ni(111) surface. The sharp molecular benzene desorption peak at ~300 K is attributed to an order/disorder transition, i.e. the breakup of the compressed superstructure by desorption of excess benzene molecules [46]. For Ru(0001), apart from a small sharp molecular benzene desorption peak at ~350 K, predominantly desorption of $D_2$ is observed which indicates dissociation of nearly the complete benzene layer (95%) upon heating [51]. Thus Ru(0001) is more reactive towards benzene dissociation than Ni(111). Desorption from Cu(111) and from Cu/Ni(111) and Cu/Ru(0001) occurs at significantly lower temperatures with no dissociation upon heating, as is concluded from the absence of a $D_2$ desorption signal. For Cu(111),
desorption is completed already at 240 K, in good agreement with the literature [60]. For Cu/Ni(1 1 1) a very similar value of 242 K is observed (the small high-temperature tail at temperatures above 240 K is attributed to desorption from surface defect sites and/or the sample holder [35]). In contrast to that, desorption from Cu/Ru(0 0 0 1) is completed only at 342 K [40], i.e. at a temperature which is around 100 K higher than on the bare Cu(1 1 1) surface and Cu/Ni(1 1 1).

The comparison of the desorption spectra of CO and benzene from Cu/Ni(1 1 1), Cu/Ru(0 0 0 1) and Cu(1 1 1) reveals that the bond strength of these two molecules is significantly increased for Cu/Ru(0 0 0 1) as compared to the two other surfaces. For benzene additional information on the adsorbate/substrate bond was obtained from recent studies, where the electronic structure of benzene was studied by ARUPS [35,36,40]. In these measurements, the bonding shift of the benzene π levels (1α2u and 1ε1g), which reflects the bonding interaction of these levels with the substrate, was determined for Cu(1 1 1), Cu/Ni(1 1 1) and Cu/Ru(0 0 0 1) and compared to those observed for Ni(1 1 1) and Ru(0 0 0 1). For benzene on Cu/Ni(1 1 1) and Cu(1 1 1) a bonding shift of only 0.2–0.3 eV was found [35], indicating a weak chemical bond. For benzene on Cu/Ru(0 0 0 1) this shift amounts to 1.1 eV [40], which is close to values of 1.3 and 1.4 eV observed for Ni(1 1 1) [61] and Ru(0 0 0 1) [62], respectively. This observation is consistent with the conclusion derived from TPD, namely that the Cu/Ni system behaves very similar to the Cu(1 1 1) surface, whereas for Cu/Ru(0 0 0 1) a significantly different behavior was observed.

3.2. Band structure determination

In order to understand the different chemical properties of the Cu monolayers on Ru(0 0 0 1) and Ni(1 1 1), we have investigated the electronic structure of these systems. For an overview, angle integrated UPS spectra of Cu/Ni(1 1 1) and Cu/Ru(0 0 0 1) are plotted in Fig. 3a and b, respectively, along with the spectra of the clean surfaces. In all cases the spectra are dominated by the emission from the d-bands, while the s- and p-states are difficult to separate from the background. Detailed inspection of the spectra reveals that for Cu/Ni the dominant emission from the Cu 3d-bands (E_f = 2.0–5.5 eV) is essentially separated from the emission from the Ni 3d-bands (0–2.5 eV). In contrast, for Cu/Ru the emission from the Cu 3d-states falls right in the center of the dominant emission from the Ru 4d-bands. This observation is consistent with the expectation that the electronic coupling of the Cu states to Ni and Ru should be different. However, in the following we will show that one has to investigate the electronic structure of the Cu monolayers much more carefully in order to understand their properties in detail.

For a better insight we have determined the k-resolved band structure of the Cu monolayers on Ni(1 1 1) and Ru(0 0 0 1) by ARUPS. The spectra were collected with the detection plane along the high-symmetry direction of the substrates, which correspond to the $\overline{T\bar{K}M}$ and $\overline{T\bar{K}T}$ direction in the surface Brillouin zone (see top of Fig. 5a and b). The azimuthal orientation of the sample was determined by LEED and azimuthal ARUPS scans, with an accuracy of better than 2°. By collecting spectra at different photon energies we are able to differentiate between two-dimensional and three-dimensional bands: for two-dimensional band structures the $E_0(k\parallel)$ data points collected at different photon energies and thus different $k\parallel$ must coincide, for bulk bands a dependence on photon energy is expected [63,64].

As an example, a series of ARUPS spectra for Cu/Ru(0 0 0 1) is shown in Fig. 4 at polar angles between 0° and 80°. The spectra have been collected with the detection plane along the [1100] azimuth (ξy-direction, Fig. 4a) and the [1120] azimuth (ξx-direction, Fig. 4b), at a photon energy of 45 eV. The Cu-derived states dominate the spectra for binding energies above 2 eV and display very characteristic dispersion. From these spectra and analogous spectra at other photon energies (Cu/Ru: 25 and 50 eV, Cu/Ni: 30, 39 and 50 eV, not shown) the $k\parallel$ dispersion of the Cu-derived bands is determined by applying a free electron dispersion relation of the final state [63,64], i.e. $k\parallel = (2m/\hbar^2 E_{Kin})^{1/2} \sin \theta$. The resulting $k\parallel$-dispersion for Cu/Ni(1 1 1) and Cu/Ru(0 0 0 1) is plotted in Fig. 5a and b, respectively for the two
Fig. 3. (a) Angle integrated UPS of a pseudomorphic Cu monolayer on Ni(111) along with the corresponding spectra for Ni(111) and Cu(111). All spectra have been collected with a photon energy of 30 eV. (b) Angle integrated UPS of a pseudomorphic Cu monolayer on Ru(0001) along with the corresponding spectra for Ru(0001) and Cu(111). The spectra of Cu/Ru(0001) and Ru(0001) have been collected with a photon energy of 45 eV, the spectrum of Cu(111) with 30 eV.

High symmetry directions in k-space, i.e. [110], [112] and [1100], [1120]. Less dominant peaks are presented by smaller symbols. The total error bars for energy and $k_{\parallel}$ values are 0.2 eV and 0.15 Å$^{-1}$, respectively.

For Cu/Ni(111) the Cu-dominated bands ($E_B < 2.0$ eV) clearly display the typical behavior of two-dimensional states. The data collected at different photon energies coincide within the margin of error. Furthermore, the periodicity of the Cu bands is in good agreement with that of the surface Brillouin zone of the Ni(111) substrate, which is particularly evident at the $\overline{\Gamma}$ point along [112] and the $\overline{M}$ point along [110]. These observations give strong evidence for a pseudomorphic Cu monolayer with a two-dimensional band structure [37].

Overall, the behavior for Cu/Ru(0001) is similar, but not as pronounced as for Cu/Ni(111). Again, the data collected with different photon energies are in good agreement within the experimental margin of error and the periodicity of the Cu-derived bands reflects that of the surface Brillouin zone of the underlying substrate. Thus, here we also have strong evidence for the formation of a pseudomorphic, two-dimensional Cu layer.

We want to mention that for Cu(111) several surface states exist at binding energies between 0 and 2 eV [30,65–68]. Due to the dominating signal from the Ni and Ru substrates and the chosen photon energies, our ARUPS measurements do however not allow to draw any conclusion on the existence of these surface states for the pseudomorphic monolayers.
Fig. 4. Series of angle resolved UPS spectra for the pseudomorphic Cu monolayer on Ru(0001) at increasing polar angles, $\vartheta$, collected at a photon energy of 45 eV and an angle of incidence of 45°. The plane of detection, $D$, was set parallel to the plane defined by the electric field vector, $\vec{E}$, of the incoming light and the surface normal ($D|\vec{E}$). (a) [1100] azimuth ($\equiv y$-direction); (b) [1120] azimuth ($\equiv x$-direction).

3.3. Comparison to slab model calculations

In order to obtain a detailed understanding of the experimental spectra and in particular for the observed difference between Cu/Ni(1 1 1) and Cu/Ru(0001) we have performed first principles slab model calculations based on DF theory. The applied code (WIEN95) uses the full-potential linearized augmented plane wave (FLAPW) technology [69,70]. The adsorption systems are modeled in two different ways: (A) Calculations are performed for an unsupported hexagonal Cu layer with a lattice constant equal to that of the Ni(1 1 1) and the Ru(0001) surface, respectively. (B) The adsorption system is modeled by a seven layer Ni or Ru slab with one Cu layer added at the position of the next substrate layer on both sides of the slab (fcc site for Ni, hcp site for Ru); this structure is repeated at a distance of four atomic layers to obtain periodic boundary conditions. The mutual interaction of the repeated slabs is negligible in this setup. The corresponding results of both calculations for Cu/Ni(1 1 1) and Cu/Ru(0001) are shown in Figs. 6 and 7, respectively, along with the experimental results from Fig. 5. In all cases the calculated band structures were down-shifted by several tenth of an eV in order to enhance the agreement with the experiment ($E_F \equiv 0$ eV). These shifts are justified by the well-known tendency in DF one-particle spectra to underestimate valence ionization energies. For the type B calculations the gaps of the projected Ni or Ru band structure are shown as well. We want to note that the calculated bulk band structure of Ru is in very good agreement with a previous study by Lindroos et al. [71].

We will first compare the calculations for the unsupported Cu layers among each other and to the experimental results. The calculations for the unsupported Cu layers with the Ni and the Ru lattice constants (Figs. 6a and 7a, respectively) reveal that the shape of the bands is very similar in both cases. The only major difference is the significantly larger bandwidth for the former: 2.9 vs. 2.0 eV at the $\Gamma$ point along [1 1 0] or [1 1 0]. This behavior is exactly what one expects from simple overlap arguments: The surface lattice constant of Ru (2.71 Å) is by 8.4% larger than that of Ni (2.49 Å), which results in smaller overlap of the Cu 3d wave functions for the Cu monolayer with the Ru lattice constant case and thus in a smaller band width. The comparison of the calculated and the experimental data leads to quite different results for the two substrates. For Cu/Ni(1 1 1) we find excellent agreement between the experimental results and the calculation for the unsupported layer throughout the Brillouin zone (Fig. 6a). This is true for the periodicity of the bands as well as the observed bandwidth and indicates that the electronic structure of Cu/Ni(1 1 1) is well described by that of an isolated Cu layer. In contrast to these results, for Cu/Ru(0001) reasonable agreement between experiment and calculation for the unsupported layer is found only at few regions in
Fig. 5. (a) $E_{\text{B}}(k_{||})$ dispersion of a pseudomorphic Cu monolayer on Ni(1 1 1) measured at photon energies of 30, 39 and 50 eV along the two high symmetry directions of the substrate ([1 1 0], [1 1 2]). (b) $E_{\text{B}}(k_{||})$ dispersion of a pseudomorphic Cu monolayer on Ru(0 0 0 1) measured at photon energies of 25, 45 and 55 eV along the two high symmetry directions of the substrate ([1 1 0 0], [1 1 2 0]). Small symbols indicate less dominant peaks.

$k$-space (Fig. 7a), e.g. at the central $\bar{T}$ point and the $\bar{T}$ point along [1 1 2 0]. These observations suggest that in contrast to Cu/Ni(1 1 1) the electronic structure of Cu/Ru(0 0 0 1) is not well represented by that of an isolated Cu layer.

In the next step we compare the experimental results with those obtained by the calculations for the full slabs (Figs. 6b and 7b). The calculated band structures are represented by the open symbols. The amount of Cu population in each $k$-resolved state is indicated by the circle radius. For the sake of clarity, states with minor (or no) Cu population are not displayed. For both systems, we find that for small binding energies (<1.5 eV) only substrate (Ni or Ru) states are seen. Moreover, for Cu/Ni(1 1 1) we find very good agreement with the experimental results for binding energies above 1.5 eV (Fig. 6b). Only at very few positions in $k$-space (i.e. at $E_{\text{B}} \sim 3.75$ eV near $\bar{I}$), we find additional states in the experiment, these states are attributed to isolated Cu atoms on top of the pseudomorphic Cu monolayer [37]. For Cu/Ru(0 0 0 1) the agreement between experiment and the full slab calculation is also quite satisfying (Fig. 7b): Throughout the Brillouin zone most of the intense experimental bands have their counterpart in the calculations. This is particularly evident for the states at 2.7 and 3.2 eV at the $\bar{T}$ point and at 2.9 and 3.9 eV at the $\bar{M}$ point along [1 1 2 0]. Nonetheless, there also is a significant
number of calculated states which do not have any counterpart in the experiment.

In the following, we will analyze the individual bands of the two systems with respect to their energetic position and symmetry with the aim to understand the observed behavior and differences in detail. In general, the coupling of the Cu-derived states to the substrate depends on the position in k-space. For Cu/Ni(1 1 1) at the $\overline{T}$ and $\overline{K}$ points most of the calculated Cu bands happen to fall into the large band gaps of the surface-projected band structure of the Ni bulk (Fig. 6b). This leads to a weak coupling between the Ni and Cu states in these regions in k-space, as is evident from the fact that both the experimental data and the calculation for the full slab are very well reproduced by the calculation for the unsupported Cu layer. The situation is quite different for Cu/Ru(0 0 0 1), where the band gaps of the surface-projected Ru bulk band structure (Fig. 7b) are observed at higher binding energies (by $\sim$1.2 eV) as compared to Ni(1 1 1). As a consequence only a few Cu 3d-states in the vicinity of the $\overline{K}$ point lie in the gap region. This leads to a significant coupling of the Cu 3d-states to the Ru states in most parts of the Brillouin zone.

The second important factor, which determines the coupling between the Cu 3d-states and the substrate states is the symmetry of the corresponding states: Coupling is only possible for states with the same symmetry. For Cu/Ni(1 1 1) there are no band gaps of the surface-projected band structure of the Ni bulk between 0 and 5 eV in vicinity of the $\overline{M}$ point (Fig. 6b). Therefore, coupling between Cu and Ni states is possible, provided the two bands have the same symmetry. This is indeed the case for the Cu $d_{xz}$ and "$d_{z^2-x^2}$" bands (denotation taken from the calculation for the unsupported layer in Fig. 6a). While the $d_{xz}$ band of the unsupported layer is of pure $d_{xz}$-character, the $d_{z^2-x^2}$ band changes its character from $d_{z^2-x^2}$ at $\overline{T}$ to $d_{x^2+y^2}$ at $\overline{M}$. Nevertheless, these two bands, $d_{xz}$ and $d_{z^2-x^2}$, are even with respect to the mirror plane defined by the surface.
normal and the [112] azimuth. They strongly interact with the bottom of the Ni d-band, states that are mainly also of d$_{x^2}$ and d$_{x^2-y^2}$ character, as well as with Ni s- and p-states. As a consequence, in this region of $k$-space the Cu-induced states in the experimental data and the full slab calculation do no longer follow the band structure of the unsupported Cu monolayer. Instead the Cu states at $E_B = 3.8$ and $2.5$ eV (at $\bar{M}$) couple to a large manifold of substrate Bloch states and consequently turn into a set of eigenstates in the energy range between $2.5$ and $4.5$ eV with minor Cu contribution in each of them. These resonance is too broad to be detected as significant photo-emission peak(s) – it only contributes to the background intensity. On the other hand, at the $\bar{M}$ points the d$_{x^2}$- and d$_{y^2}$-states of the unsupported Cu monolayer ($E_B = 1.9$ and $2.5$ eV) are odd with respect to the mirror plane ([112] azimuth). Therefore they cannot couple to the Ni states that are still even in this energy range (the odd states occur at binding energies below 1.5 eV) and the corresponding Cu bands are not significantly influenced by the presence of the Ni substrate.

Apparently, for Cu/Ru(0001) the situation is substantially different (Fig. 7b). Due to the fact that the majority of Cu states does not fall in the region of the Ru band gaps, we observe strong coupling between the Cu and Ru states in most regions in $k$-space. The calculations reveal a large number of energetically close lying Cu states that originate from the interaction with various Ru states of appropriate symmetry and which would emerge into a broad manifold of states, if the calculations could be performed for an infinitely large slab. Due to this large number of states it is – in contrast to Cu/Ni(111) – very difficult to follow the dispersion of the individual bands; they simply cannot be separated in the ARUPS spectra; instead one observed broad peaks as the sum of the individual bands. Examples for this behavior are the bands at 2.9 and 3.9 eV at the $\bar{M}$ point, which
both represent the center of gravity of several states.

One aspect that also has to be considered are symmetry selection rules. Our measurements have been performed with linearly polarized synchrotron radiation (polarization 80–85%) with the plane of detection, \( D \), always parallel to the electric field vector, \( \vec{E} \), of the incoming light \( \langle D \parallel \vec{E} \rangle \).

No strict symmetry selection rules are applicable along the \([1\bar{1}0]\) and \([1\bar{1}00]\) azimuths of Ni(111) and Ru(0001) in Figs. 6b and 7b, respectively, because the vertical planes along these directions (\( \equiv \gamma \)-direction) are no symmetry planes for the two substrates. Thus all states should be observable in this direction. The situation is quite different along the \([112]\) and \([1120]\) azimuths (i.e. along \textit{TMT}, where the crystals are symmetric with respect to the detector plane). The states can be subdivided in \textit{even} and \textit{odd} states – with our experimental setup \( \langle D \parallel \vec{E} \rangle \) the \textit{odd} states are symmetry forbidden and only the \textit{even} states can be observed. As a consequence, the odd \( d_{xy} \) and \( d_{yz} \) states are allowed along \([1\bar{1}0]\) and \([1\bar{1}00]\) but are forbidden along \([112]\) and \([1120]\). All remaining bands are allowed in both directions. The experimental results for both surfaces confirm these predictions. The small intensities of the \( d_{xy} \) states (small symbols) in the forbidden direction at the \( M \) points of both surfaces are attributed to the incomplete polarization of the synchrotron radiation.

Finally we want to address briefly the question of the binding energy of the Cu layer on the two substrates. From the calculations we find that the total binding energies per Cu atom in the pseudomorphic monolayer are identical within 0.01 eV. In view of the stronger coupling of the Cu 3d-states to the Ru states as compared to the Ni states this result appears surprising at first sight. If one splits the binding energy into different contributions, one finds that the vertical interaction of Cu to the substrate is indeed stronger by 0.25 eV for Ru as compared to Ni, as one would expect. However, this is compensated by the energy necessary to expand the Cu monolayer by +6.0% on Ru(0001) as compared to the slight compression by –2.6% of the Cu monolayer on Ni(111). Apparently, some sort of bond order con-

4. Summary and conclusions

Summarizing the comparison of the experimental results and the model calculations for the unsupported layer and the full slab model we come to the following conclusions: For Cu/Ni(111) we observe only weak coupling between the Cu 3d-states and the substrate states, due to the fact that the Cu bands partly fall into the band gaps of the projected bulk band structure of Ni and partly due to the fact that the Cu and Ni states have different symmetry. For Cu/Ru(0001) we observe strong coupling between Cu and Ru states throughout the Brillouin zone. This is due to the larger number of Ru states in the energy range of the Cu states and the fact that the band gap of the Ru substrate states are located at a lower binding energy. Based on these results we now can understand the different reactivity of the two systems. For Cu/Ni(111), the coupling to the substrate is weak and the surface therefore very much behaves like the surface of a Cu(111) crystal, even though the lattice constant is slightly compressed by 2.4%. For Cu/Ru(0001) we observe a strong coupling to the substrate with an expansion of the lattice constant relative to Cu(111) by 6.0%. Thus the electronic structure of the Cu monolayers significantly differs from that of a Cu(111) surface and also from that of Cu/
Ni(1 1 1). These changes are made responsible for the changes in the reactivity of the surface towards adsorption of CO and benzine.

Acknowledgements

This work has been supported by the BMBF through grant 05 SF8 WEA 7. The authors would like to thank Prof. Dr. D. Menzel and Dr. W. Widdra for the cooperation and support when using their photoelectron spectrometer. UB was supported by the DFG via the SFB 338. He would also like to thank Prof. Rösch for his continuous support and for providing the computer facilities.

References