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Evolution of the electronic structure in epitaxial Co, Ni, and Cu films

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Recently, electronic structure and band width of the system 1.2 monolayers Ni/Cu(100) have been found to be Ni-bulk-like [Mankey *et al.*, Phys. Rev. Lett. **78**, 1146 (1997)]. Therefore, we have traced the development of the electronic structure with thickness for various $3d$ transition metals using angle-resolved photoemission. All studied systems show similar behavior. We find, in contrast to the previous report, a very different electronic structure for the monolayer and for bulk. Moreover, our measured binding energies support the results of local-density calculations which obtain strong narrowing of the $3d$ band width of 1 monolayer Ni/Cu(100) as compared to bulk Ni.

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Low-dimensional materials have been attracting both experimental and theoretical interest due their peculiar physical properties which can differ significantly from those of materials with higher dimensionality. So-called finite-size effects occur when a structure is restricted in one dimension, this is, e.g., the case when the thickness of a film decreases down to atomic dimensions corresponding to a transition from three-dimensional to two-dimensional behavior. In this case the electronic band width becomes narrower due to an atomic coordination reduced with respect to the one of the bulk. This can be quantified as $W \propto \sqrt{n}$ in the tight-binding model, where W is the valence band width and n the number of nearest neighbors, and has been confirmed in countless calculations of the electronic structure of crystal surfaces, free-standing monolayers, and monolayers on weakly interacting substrates such as noble metals.

A well-established method to experimentally investigate the electronic structure of bulk systems, surfaces, and thin films is angle-resolved photoemission.[1] Mankey *et al.*[2] have recently employed angle-resolved photoemission to study the electronic structure of Ni/Cu(100) films. Reference 2 reports that electronic structure and band width of atomically thin Ni films [1.2 monolayer (ML) on Cu(100)] do not differ from those of bulk Ni.[2] This finding is based on angle-integrated photoemission spectra and on photoelectron angular distribution patterns for a narrow energy window around the Fermi energy obtained with a display-type analyzer.[3] It has been interpreted as a hybridization and charge-transfer effect between Ni and Cu through which the Ni monolayer develops the characteristics of a bulk electronic structure.[2] Similar behavior has also been observed in atomically thin Cu/Ni(100) and Co/Cu(100) films.[2]

We are not aware of any corroboration or rejection of this surprising finding, with the exception of an x-ray-absorption study which notes that from absorption spectra 1 ML and 5 ML Ni/Cu(100) can be well distinguished as the density of unoccupied $3d$ states is by 20% larger for 1 ML than for 5 ML.[4] Band theory has early on predicted for 1 ML Ni/Cu(100) a reduced magnetic moment[5–7] ($0.37\mu_\mathrm{B}$ in Ref. 5; $0.24\mu_\mathrm{B}$ in Ref. 7; the bulk Ni value is $0.59\mu_\mathrm{B}$ in Ref. 8), which can be explained by band narrowing.[7] The development of the band structure of Ni/Cu(100) with thickness has been studied and quantized states have been identified up to at least 15-ML Ni by inverse photoemission,[9] but no systematic study has been reported for occupied states. We have therefore reinvestigated the development of the electronic structure in epitaxial Co, Ni, and Cu films by angle-resolved photoemission. In this paper we show that the electronic structure of atomically thin films is not bulklike, in contrast to the result of Ref. 2. In addition, the angle-resolved spectra allow us to trace the evolution of the electronic structure with thickness.

Angle-resolved photoemission experiments have been performed at the TGM 5 undulator beamline at the BESSY I storage ring in Berlin. The synchrotron light was incident at an angle of about 30° for normal-electron-emission geometry. This leads to a mixed (s and p) light-polarization geometry. A 90° spherical analyzer with an energy resolution of about 200 meV at an angular acceptance of 1° has been used. The spectra for different thicknesses were taken at normal emission with a photon energy of 43 eV because this correponds for the present fcc materials to the Γ point along [100] for binding energies near E_F.

The Cu(100) crystal has been prepared by sputtering and annealing (600 °C) cycles. The base pressure of the vacuum system was 1×10^{-10} mbar. The various overlayers have been produced *in situ* by e^--beam evaporation onto Cu(100) at room temperature. The pressure rose to a maximum of 5×10^{-10} mbar during the Co, Ni, and Cu evaporations. Evaporation rates have been measured with a quartz-crystal microbalance, and the quartz reading was used for thickness calibration. The materials were deposited at a typical rate of 0.5–1 Å/min. All systems show epitaxial growth at room temperature, but the growth modes of the various systems differ in detail: Between fcc Co and Cu there is only a small lattice mismatch. Reflection high-energy electron diffraction oscillations have been observed up to 40 ML for Co/Cu(100).[10] Scanning tunneling microscopy (STM) (Refs. 11–13) shows that the growth occurs in a layer-by-layer mode of high quality above 2 ML up to at least 15 ML.

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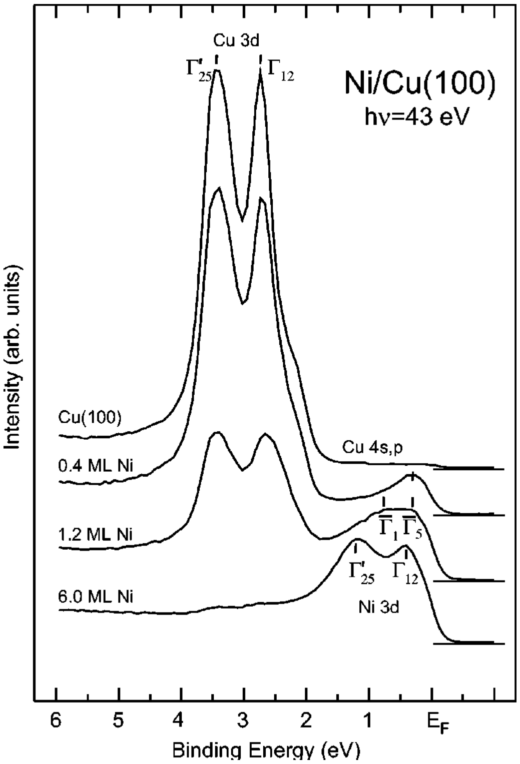

FIG. 1. Angle-resolved photoemission spectra of the valence band. Normal-emission spectra in the vicinity of the Brillouin-zone center of Cu(100) and selected coverages of Ni/Cu(100).

Below 2 ML nominal coverage, a substantial amount of simultaneous bilayer growth has been reported,[12,14] but its extent is still under discussion.[13] In an STM study of Ni/Cu(100),[15] nearly perfect submonolayer growth and very good layer-by-layer growth up to 3.4 ML has been reported. There are indications for subsurface growth of the first Ni monolayer on Cu(100) at room temperature from x-ray photoemission and CO adsorption behavior[16] and from low-energy electron diffraction (LEED) (Ref. 17) supported by recent first-principles total-energy calculations.[18] Cu grows on Co/Cu(100) (Ref. 10) and on Ni/Cu(100) (Ref. 19) in an epitaxial layer-by-layer mode. Therefore, we have used 8 ML Ni/Cu(100) and 10 ML Co/Cu(100) as Ni(100) and Co(100) substrates, respectively. In the present work, the surface order has been checked by LEED. A sharp $p(1\times1)$ LEED pattern and low background intensity have been observed in all preparation stages for all systems [0–8 ML Ni/Cu(100), 0–2.8 ML Cu/Ni(100), 0–10 ML Co/Cu(100), and 0–2.6 ML Cu/Co(100)] confirming good structural order in the topmost surface layer.

The spectra in Fig. 1 reveal the dependence of the Ni electronic structure on the overlayer thickness. We show complete valence-band spectra of Cu(100) and of 0.4, 1.2, and 6 ML Ni/Cu(100) at arbitrary normalization. Regions of Ni3d and Cu3d emission can easily be distinguished as the pure Cu spectrum shows at 43-eV photon energy no feature between 2 eV and the Fermi level. Cu3d emission occurs between 2 and 4 eV. The peak at 2.7-eV binding energy originates from the Δ_1 band (Γ_{12}), and the second peak at 3.4-eV binding energy from the Δ_5 band (Γ'_{25}). The shoulder at 2-eV binding energy is due to Cu4s,p emission.

In the spectrum of 0.4 ML Ni, a single peak is observed at 0.3-eV binding energy. At larger thickness of 1.2 ML, a second peak appears at 0.8-eV binding energy. For the 6-ML Ni film, two peaks derived from Ni3d states are observed at 0.4 and 1.2-eV binding energy. Only a very weak feature due to emission from the Cu3d band is seen between 2 and 4-eV binding energy. This is a clear indication that the Cu substrate is covered almost completely by 6-ML Ni.

For a more detailed discussion we turn to Fig. 2, which displays the energy region of the 3d photoemission of Co, Ni, and Cu films for smaller thickness intervals. The peaks marked in Fig. 1 and Fig. 2(a) contain contributions from both spin directions. They are not resolved since the exchange splitting in Ni is small (experimentally 0.15 eV for bulk Δ_1, near the Γ point[20]). Energy positions obtained for 1 ML are 0.3 and 0.75 eV. The energy positions agree with published photoemission measurements on 1 and 2 ML Ni/Cu(100) at normal emission.[21] The present work goes beyond Ref. 21 in the sense that larger thicknesses are reached in Fig. 2(a) and that the spectra have been measured near the Γ point. Therefore, we can observe that energy positions close to those of bulk states are already reached at 3 ML. The Ni bulk band structure has an extremum in binding energy at a photon energy of 44 eV corresponding to the Γ point for 3d-derived states. The peak at 0.4-eV binding energy for 3–10 ML originates from the Δ_1 band (Γ_{12}) and the feature at 1.2-eV binding energy originates from the Δ_5 band (Γ'_{25}).

Figure 2(b) shows the case of fcc Co/Cu(100). The bulk exchange splitting of fcc Co is large-experimentally 1.55 eV at Γ'_{25} (Ref. 22). Still, we observe one peak less than in Fig. 2(a). This is due to the following reasons: (i) Co has a lower number of 3d electrons than Ni which shifts energy positions upwards and (ii) the majority-spin peak of Δ_5 (Γ'_{25}) is broad, and it is difficult to determine its energy position even in spin-resolved spectroscopy. Therefore, the peak marked in Fig. 2(b) is of minority spin and develops into $\Gamma'^{\downarrow}_{25}$ [experimentally at 0.9 eV (Ref. 22)]. For 1 ML, more than one peak at 0.45 eV cannot be assigned with certainty. In case of substantial bilayer growth[12–14] it can indeed be expected that distinction of 1 from 2 ML in the spectra becomes difficult.

In Fig. 2(c), we show Cu/Ni(100) and take advantage of the comparatively narrow width of 3d peaks in Cu and of the absence of exchange splitting. Below 1 ML, one peak is seen at 2.75 eV. Around 1 ML, peaks appear at 2.8 and 3.2 eV. Based on calculations of Cu monolayers, e.g., Ref. 23, the higher-binding-energy peak is assigned to $\bar{\Gamma}_1$ and the lower-binding-energy peak to $\bar{\Gamma}_5$. Towards larger thicknesses the peaks move closer together until around 1.5 ML they cannot be separated from each other at the present resolution. At 2 ML, peak positions (3.35 and 2.95 eV) are not too far from the ones of bulk Cu [3.6 and 2.9 eV from pure Cu(100) at the top of Fig. 2(c)]. Note that the order of odd- and even-symmetry states is reversed for monolayer and for bulk, thus the mutual approach of peaks around 1.5 ML likely marks a crossing over of states. It is possible that for Ni/Cu(100) and Co/Cu(100) this is not observed very well due to a tendency

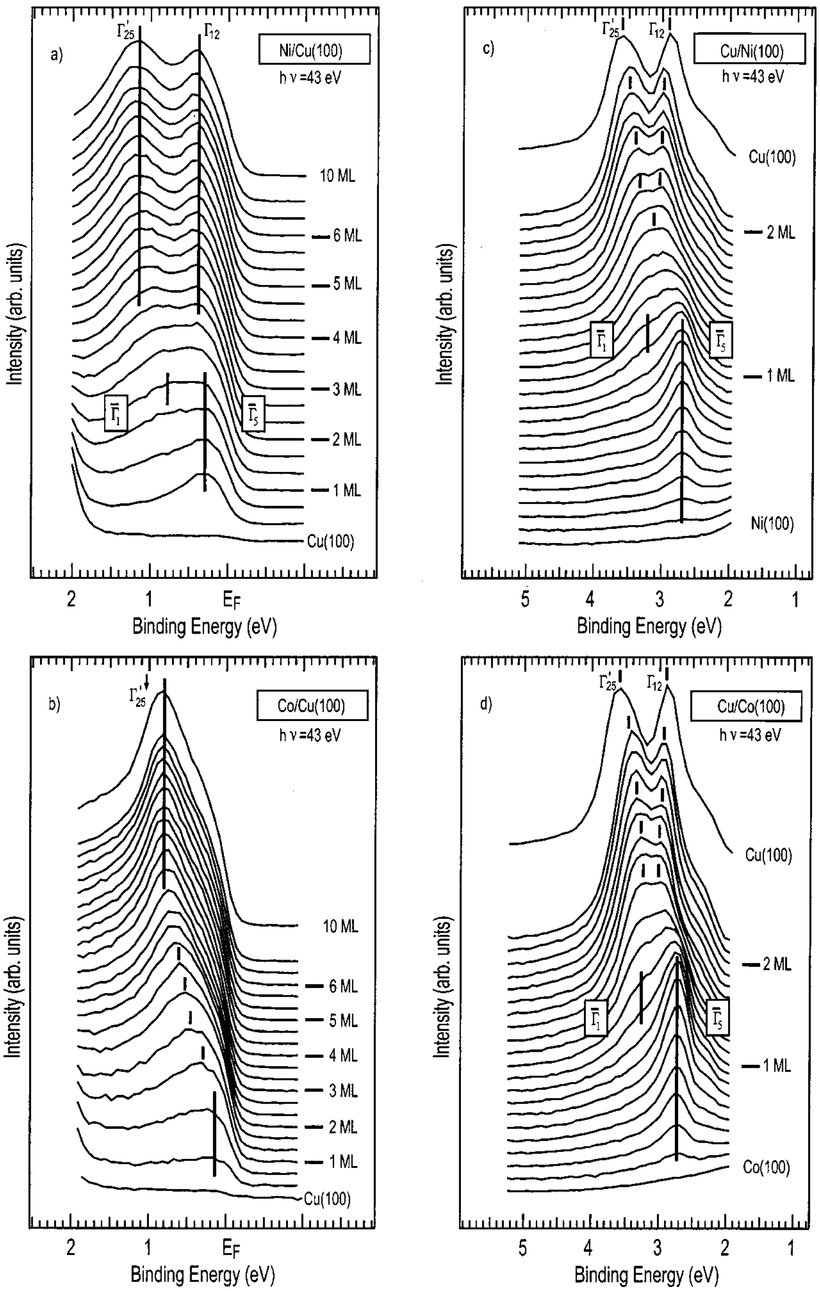

FIG. 2. Spectra showing the energy range of $3d$ emission in detail. All systems show similar behavior with film thickness.

for bilayer growth below 2 ML thickness as observed for Co/Cu(100) and a possible tendency for subsurface growth of Ni/Cu(100).

The situation in Fig. 2(d) for Cu/Co(100) is similar. Spectra resemble the ones of Ref. 24, Fig. 4, measured at 50-eV photon energy. Binding energies in Fig. 2(d) are 2.75 eV for thicknesses below 1 ML and 2.8 and 3.25 eV at 1 ML. The merging of peaks between 1 and 2 ML is somewhat less pronounced than for Cu/Ni(100) in Fig. 2(c). Measured energy positions have been summarized in Table I.

We want to discuss the relevance of the present data for assessing the band width of Ni/Cu(100). All calculations find a substantial narrowing of the $3d$ band width for the Ni monolayer. It has been quantified as being by 30% narrower for the free Ni(100) monolayer.[26] Also on Cu(100), 1 ML Ni has with a FWHM of just 1.6 eV[5] a very narrow $3d$ band,[6]

TABLE I. Peak positions determined in the experiment (binding energies in eV).

Thickness	Ni/Cu(100)	Co/Cu(100)	Cu/Ni(100)	Cu/Co(100)
1 ML	0.75 ($\bar{\Gamma}_1$), 0.3 ($\bar{\Gamma}_5$)	0.3 ($\bar{\Gamma}_1^{\downarrow}$)	3.2 ($\bar{\Gamma}_1$), 2.8 ($\bar{\Gamma}_5$)	3.25 ($\bar{\Gamma}_1$), 2.8 ($\bar{\Gamma}_5$)
Bulk	1.2 (Γ_{25}'), 0.4 (Γ_{12})	0.8 ($\Gamma_{25}'^{\downarrow}$)	3.6 (Γ_{25}'), 2.9 (Γ_{12})	3.6 (Γ_{25}'), 2.9 (Γ_{12})

which is also narrower than the density of states of the interior Cu planes.[7] We can compare our measured peak positions to the energy eigenvalues given in Refs. 5 and 7. The lowest measureable states in normal emission are $\bar{\Gamma}_1$ at 0.75 eV for 1 ML and Γ'_{25} at 1.15 eV for 6 ML. Experimental literature values for Γ'_{25} range from 1.1 to 1.2 eV.[25] Due to the particularly strong electron correlation in Ni, these values are much closer to the Fermi energy than energy eigenvalues from local-density theory, which range for Γ'_{25} from 1.97 to 2.15 eV (Ref. 25). This correlation effect has to be considered in addition to the finite-size effect we are discussing here. Local-density theory gives for $\bar{\Gamma}_1^{\uparrow}$ of 1 ML Ni/Cu(100) 1.13 eV (Ref. 7) and 1.16 eV (Ref. 5) (minority-spin values are not given in Ref. 7). If we assume the same effect on $\bar{\Gamma}_1$ as on Γ'_{25}, we expect from photoemission a value around 0.65 eV for $\bar{\Gamma}_1$. This is very near to our experimental value of 0.75 eV. Thus, the behavior of the deepest measureable state at $\bar{\Gamma}$ and Γ with thickness, which changes from 0.75 to 1.15 eV from 1 to 6 ML in our experiment, is obviously well described by the theoretical change from 1.1 to 2 eV when electron correlation is taken into account. In this way, the experimental data corroborate local-density theory, which obtains strong narrowing of the $3d$ band width in 1 ML Ni/Cu(100) with respect to bulk Ni.

We conclude that the electronic structure of all films studied reveals a strong dependence on thickness, including Ni/Cu(100). All systems show similar behavior with respect to the evolution of the electronic structure with thickness. States are probed simultaneously at $\bar{\Gamma}$ for monolayers and Γ for thicker layers, and by comparison to local-density theory, it is concluded that the band width increases substantially in going from monolayer to bulk. This corroborates the view that the dimensionality of transition-metal noble-metal overlayer systems mainly determines the character of the electronic states. Compared to this, the effect of hybridization should be negligible.

The results presented for the occupied electronic structure indicate that the electronic structure at the Fermi energy must also be different for the monolayer and thicker layers. This holds even more as the strong changes that the unoccupied electronic structure of Ni/Cu(100) undergoes with thickness have already been observed.[9] The difference in conclusion between Ref. 2 and the present work might be connected to differences in thickness calibration. We see from Fig. 2(a) (e.g., the spectrum of 2.3 ML) that this difference does not need to be large. An underestimation of the thickness by one monolayer in Ref. 2 might be sufficient to explain the differences in conclusion.

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