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Electronic properties of body-centred-tetragonal copper

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Abstract. Angle-resolved photoemission with synchrotron light is used to determine the band structure of five- and six-layer films of Cu grown epitaxially on Pd{001} and on Pt{001}. The films have body-centred-tetragonal structure resulting from the large plane strains of 8 to 9% imposed by the substrates. The band structure is the same, within experimental error, for films grown either on Pd{001} or Pt{001}, and is similar to that of stable FCC Cu.

1. Introduction

We have recently shown that thin films of Cu with thicknesses up to 10 layers can be grown epitaxially and pseudomorphically on Pd{001} [1] and on Pt{001} [2] at room temperature with body-centred tetragonal (BCT) structure ($a = 2.75$ Å on Pd{001}, $a = 2.78$ Å on Pt{001} and $c = 3.24$ Å in both cases). The equilibrium (i.e., the unstrained) phase of the grown Cu film was shown to be the stable FCC structure (lattice constant $a_0 = 3.61$ Å), despite the large misfit to both the Pd substrate ($a_0 = 3.89$ Å, hence misfit of 7.8%) and the Pt substrate ($a_0 = 3.93$ Å, hence misfit of 8.9%). The growth of coherent films thick enough to permit the determination of bulk spacings under such remarkably large plane strains was wholly unexpected, and offers the rare possibility of studying the atomic and electronic properties of non-equilibrium crystalline phases. The atomic structure of the strained Cu films was determined with low-energy electron diffraction (LEED) [1, 2] and was found to be essentially the same on either the Pd or the Pt substrate. It is the purpose of the present investigation to determine the electronic structure of these films by means of angle-resolved photoemission spectroscopy (ARPES).

Section 2 gives experimental details, section 3 presents the results and section 4 summarizes the conclusions.

2. Experiment

The experimental procedures followed for the preparation of either substrate surface (Pd{001} and Pt{001}) and for the growth of the Cu films are described in detail elsewhere [1,2]. Here we mention only that the Cu source was a Cu wire wrapped

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on a W filament which was heated electrically and located approximately 30 cm away from the substrate. The deposition rate was about one layer in 10 to 15 min.

The photoemission experiments were carried out at beamline U7B of the National Synchrotron Light Source in the Brookhaven National Laboratory. The samples were mounted on a 3-axis manipulator that allows photoemission experiments with either s- or (75% s+25% p)-polarized light [3]. The synchrotron light was dispersed with a plane grating monochromator and the energies of the photoemitted electrons were measured by means of an angle-resolved double-pass cylindrical mirror analyser with an angular resolution of 2°. The combined energy resolution of monochromator plus analyser was estimated to be 0.35 eV at 100 eV.

The orientation of the sample with respect to the light beam was fixed as follows. Consider a right-handed coordinate system x, y and z, with the Poynting vector of the incident light collinear with the x axis and the electric vector collinear with the y axis: in the case of s-polarization the surface normal n was at an angle of 43° to the z axis and its projection n_{xy} on the x, y plane was antiparallel to the x axis; in the case of 25% p-polarization the surface normal was still at 43° to the z axis, but its projection n_{xy} formed an angle of 130° with the x axis.

All measurements were done on electrons emitted in the direction of the surface normal (so-called normal emission).

3. Results

Angle-resolved electron-distribution curves (EDCs) measured at normal emission with (75% s+25% p)-polarized radiation and photon energies $h\nu$ ranging between 14 and 165 eV are shown in figure 1 for a Cu film approximately six layers thick grown on Pt{001} and in figure 2 for a Cu film approximately five layers thick grown on Pd{001}.

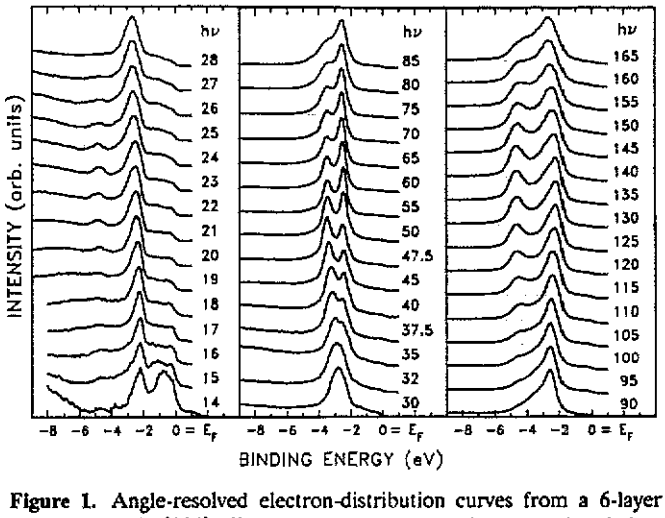

Figure 1. Angle-resolved electron-distribution curves from a 6-layer film of Cu grown epitaxially on Pt{001}. The curves were measured at normal emission with 75%s+25%p-polarized radiation with the photon energies $h\nu$ as indicated.

The large emission observed for small $h\nu$ values at binding energies between the Fermi level (E_F) and about -2 eV has contributions from the substrate buried under the Cu film and will therefore not be discussed further here. The peak located at -2.2 eV for $h\nu = 14$ eV is due to the Δ_5 band of the Cu film and disperses visibly with photon energy, reaching a maximum binding energy of -3.5 eV at about $h\nu = 60$ eV (Γ point). A new peak appears above $h\nu \approx 30$ eV at -2.6 eV which reaches a minimum in binding energy of -2.2 eV at 130 eV (X point). At $h\nu \sim 55$ eV this peak has contributions from both the Δ_1 and the Δ_2 bands, while at $h\nu \sim 130$ eV it has contributions from both the Δ_2 and the Δ_5 bands.

Low photon energies produce a smaller emission peak at -4.8 eV that exhibits no dispersion below 30 eV and reaches a maximum intensity at $h\nu = 23$ eV. The difference in the intensities of this peak between figure 1 and figure 2 is ascribed to the fact that the film grown on Pt{001} was about 20% thicker and had more defects, on account of the larger misfit, than the film grown on Pd{001}. This peak is p sensitive (see below) and is similar to the surface state which has been observed on FCC Cu{001} [6]. It may be due to a surface state [1] as well, but it has also a partial contribution from the top of the lower Δ_1 band, as demonstrated by the dispersion of this band for photon energies larger than 30 eV (more clearly visible in figure 2). The maximum in intensity at $h\nu = 23$ eV may be a further confirmation of the contribution from the surface state because, whereas the intensity of the surface-state peak is expected to increase when the photon energy decreases to reach the X point [7], the contribution of the surface state to the EDCs decreases when the mean free path of the photoelectron increases with decreasing photon energy. We should note here that the emissions from the surface state and from the lower Δ_1 band could *not* be observed on clean FCC Cu{001} at normal emission with photon energies smaller than 40 eV. This difference is probably due to the fact that in the present experiments the Cu film had a BCT, not FCC, structure.

For larger photon energies ($h\nu$ values between 100 and 165 eV) stronger emission occurs at -4.6 eV, but this peak disperses and is probably due to emission from the Δ_2' band. The limited resolution of our monochromator did not allow us to decompose this peak into its components. The polarization dependence of these peaks is demonstrated in figure 3. The emission at -4.8 and -4.6 eV is clearly p-sensitive (bottom curves at $h\nu = 23$ eV and top curves at $h\nu = 130$ eV), but at high photon energies there is also an s-sensitive contribution which is probably due to the Δ_2' band. With $h\nu = 60$ eV (at the Γ point) two peaks are observed (middle curves in figure 3), the lower-binding-energy peak has contributions from both the upper Δ_1 band and the Δ_2 band, whereas the higher-binding-energy peak is predominantly s-sensitive and is assigned to the Δ_5 band.

The experimental data presented in figures 1 and 2 have been used to construct an experimental band structure of the strained Cu films. The procedure followed for this purpose was to assume as valid the free-electron parabolic relation between energy and momentum,

$$k_{f\perp} = 0.512(h\nu + E_F - E_b)^{1/2} \tag{1}$$

where: $k_{f\perp}$ = final-state momentum perpendicular to the surface inside the crystal, in Å^{-1}; $h\nu$ = photon energy, in eV; E_F = Fermi energy, with respect to the bottom of the band (4 eV [4]); and E_b = positive binding energy below E_F, in eV.

The data obtained with this procedure are shown as circles in figure 4, for Cu/Pd{001} on the left and for Cu/Pt{001} on the right, and compared to the band

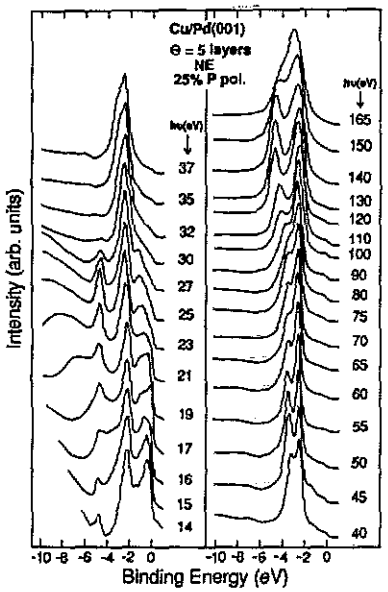

Figure 2. Angle-resolved electron-distribution curves from a 5-layer film of Cu grown epitaxially on Pd{001}. The curves were measured at normal emission with 75%s+25%p-polarized radiation with the photon energies $h\nu$ as indicated.

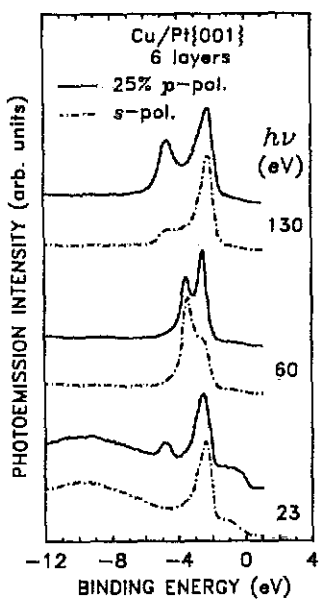

Figure 3. Polarization dependence of normal photoemission from a 6-layer Cu film on Pt{001} with $h\nu = 23$, 60 and 130 eV.

structure of FCC Cu as calculated by Moruzzi [5] (solid curves in figure 4). Note, however, that in these plots the distance between Γ and X has been expanded to fit the periodicity along the direction normal to the {001} surface as determined by

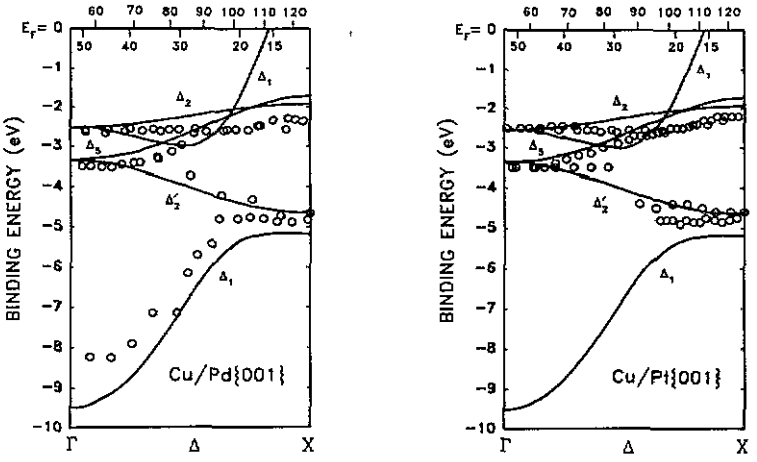

Figure 4. Experimental band structure (circles) of strained FCC (body-centred-tetragonal) Cu along the ΓΔX line. The numbers on top of the two panels refer to final-state energies. *Left: Cu film grown on Pd{001}. Right: Cu film grown on Pt{001}.* The solid curves are calculated for bulk (unstrained) FCC Cu.

LEED (3.24 Å) rather than that of stable bulk FCC Cu (3.61 Å). Nevertheless, the comparison between experiment and calculated band structure has only qualitative validity because the calculation was done for the equilibrium, i.e., the unstrained, phase of FCC Cu.

We note that the results are essentially the same for the two Cu films grown on the two substrates, a confirmation of the LEED results reported elsewhere [1,2]. The data from the Cu/Pd{001} film allowed the determination of the lower Δ_1 band, whose emission was too weak in the Cu/Pt{001} film, probably because of the larger strain. We note also that the dispersions of the Δ_2 and the Δ_5 bands are consistent with Moruzzi's calculation for FCC, *not* BCC, Cu (see figure 3 of [8]), again in agreement with the LEED results.

4. Conclusions

We have determined the band structure of a body-centred-tetragonal modification of Cu, as obtained by epitaxial growth on either Pd{001} or Pt{001}. This modification is a highly strained (8 to 9%) form of the stable FCC Cu structure at room temperature, and is essentially the same for Cu films grown either on Pd{001} or Pt{001}.

One may wonder why the equilibrium phase is FCC Cu, despite the very large lattice mismatch, rather than BCC Cu, for which total-energy calculations as a function of volume [9–11] predict a lattice constant of 2.88 Å and hence a much smaller lattice mismatch. The experimental evidence is indisputable: a LEED structure determination combined with strain analysis [1,2,12] has demonstrated that the equilibrium phase *cannot* be BCC. The theoretical explanation is the following: a total-energy calculation on tetragonal distortions of Cu around the BCC structure shows that the BCC structure is unstable [13]. Hence, stabilization of the BCC lattice by pseudomorphic epitaxy on either Pd or Pt{001} is not expected to be successful: perhaps because of its remarkable softness, very thin films of Cu on these substrates prefer to grow with a

tetragonally distorted structure of the FCC phase, despite the large lattice mismatch with the substrates.

The experimental band structure of these films is similar to the band structure calculated for bulk FCC Cu. In the absence of a band-theoretical calculations a detailed explanation for this finding is not available at this time, but the result itself seems reasonable: we note that the tetragonality of the structure is not large, only 17% away from the FCC structure ($c/a = 0.83$ for Cu/Pd{001} versus $c/a = 1$ for FCC Cu), and the number of d electrons in BCT Cu is essentially the same as in FCC Cu.

In any case, it would be very desirable to compare the present experimental results with those of (as yet unavailable) theoretical calculations of the band structure of body-centred tetragonal Cu. The present results reveal also the presence of a p-sensitive photoemission peak at about 4.8 eV below the Fermi level which may due to a surface state.

Acknowledgments

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