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Epitaxial growth of body-centered-tetragonal copper

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Deposition of Cu in ultrahigh vacuum on a clean Pd{001} surface leads to the growth of a new crystalline Cu phase with body-centered-tetragonal (bct) structure well ordered up to about 10 layers. A low-energy electron-diffraction (LEED) analysis of 6-layer films finds the bulk lattice parameters to be $a=2.75$ Å and $c=3.24$ Å, with little relaxation of the surface layers. Photoemission experiments confirm that the grown phase is different from the stable fcc modification and show a surface state 4.8 eV below the Fermi energy which is not present in fcc Cu. The grown phase may correspond to a theoretically predicted bct phase under slight strain, but we also show directly that it is probably strained bct and not strained bcc or fcc.

A recent first-principles total-energy calculation, by Morrison, Kang, and Mele (MKM),[1] of body-centered-tetragonal (bct) Cu as a function of a, the side of the square cross section, and c, the height of the bct cell, produced a remarkable result. The calculated energy shows, as expected, a minimum at the face-centered-cubic (fcc) structure ($a=2.55$ Å, $c=3.61$ Å) (Ref. 2) and a minimum at the body-centered-cubic (bcc) structure ($a=c=2.86$ Å) (Ref. 3) with energy 4.8 mRy/atom higher than the fcc minimum, but also a minimum at an intermediate tetragonal structure ($a=2.76$ Å, $c=3.09$ Å) (Ref. 4) with energy 3.2 mRy higher than the fcc minimum. MKM labeled this new tetragonal phase α-bct and predicted that it may possibly be grown on a cubic substrate with a lattice constant of 2.76 Å.

We became interested in this new bct phase because fcc Pd, with cubic lattice constant $a_0=3.89$ Å, has a square surface mesh on its {001} faces with sides $a=2.75$ Å, and hence appears favorable for epitaxy of the predicted α-bct phase of Cu. We had previously been quite successful in growing Mn epitaxially on Pd{001},[5] but only partially successful in growing Cu on bcc Fe{001}.[6]

We prepared a clean Pd{001} surface and deposited on it, in an ultrahigh vacuum environment, Cu films with different thicknesses. We studied these films with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and angle-resolved photoemission spectroscopy (ARPES), and we report below the results of these studies. We describe first the experiments, then the LEED observations and analysis, and finally some of the ARPES results. We limit ourselves here to the LEED analysis of multilayer Cu films, postponing the description of the early stages of film growth and the full evaluation of the ARPES data to a later time.

The palladium substrate, a Pd platelet with a polished {001} surface exposed, was cleaned in ultrahigh vacuum with a series of argon-ion bombardments and oxygen treatments, to reduce the carbon concentration, as described elsewhere.[5] The deposition source was a Cu wire wrapped on a W filament which was heated by passage of an electric current and located approximately 30 cm away from the substrate. The substrate was not heated during film growth. With the source at 850–900 °C the deposition rate of Cu was about 1 layer in 15 min. The thickness of the Cu films was determined by measuring the ratio of the intensity of the Cu AES signal at 920 eV to that of the Pd AES signal at 330 eV and using standard formulas (see, e.g., Ref. 7) with inelastic mean-free paths $\lambda_{330}=5.4$ Å and $\lambda_{920}=10.8$ Å as calculated by Penn.[8] The conversion of thickness in Å to thickness in number of Cu layers was done by means of the relation (justified *a posteriori* by the results of the LEED analysis): 1 Cu layer equals 1.6 Å.

The clean Pd{001} surface produced a sharp, low-background, 1×1 LEED pattern. Deposition of Cu did not affect the geometry of the pattern—no extra beams appeared; i.e., the surface unit mesh remained 1×1, but the background increased gradually with coverage. For film thicknesses of 1–2 Cu layers the background could still be classified as low, but for 10-layer films the diffracted beams were broad and diffuse and the background high, while for 20-layer films the LEED pattern was almost completely obliterated. These qualitative observations, together with the knowledge provided by AES about the thickness of the Cu deposits, indicate that the films thinner than about 10 layers were predominantly crystalline and pseudomorphic, but thicker films were highly disordered.

Measurement of the LEED intensity spectra revealed large changes with coverage in the initial stages of Cu deposition, but as soon as the films reached a thickness of 4–5 layers all spectra became stable, i.e., independent of film thickness. These spectra were very different from those of either clean Pd{001} or clean Cu{001}, announcing a new crystalline phase. In order to determine the parameters of this new phase we carried out a LEED intensity analysis. Note, though, that, owing to experimental limitations, the data base is limited: only four LEED spectra could be measured, namely, 10, 11, 20, and 21, at normal incidence, and only the first three were considered sufficiently reliable to be included in the analysis. Three sets of data were recorded, one from each of three Cu films, independently prepared on clean Pd{001} surfaces, with three different thicknesses, namely, 4, 5, and 6 layers. All data were normalized to constant incident electron current, the background was subtracted and the curves were smoothed. The three sets, presented in Fig. 1 (solid curves), confirm the stability of the spectra with respect to film thickness.

The intensity calculations were done with the CHANGE computer program.[9] For the analysis, the Cu films were assumed to be semi-infinite (see below for a test of the validity of this assumption). The Cu potential was taken from the compilation of Moruzzi, Janak, and Williams,[10] the calculations included 8 phase shifts and 45 beams. The root-mean-square amplitude of atomic vibration was set at $\langle\langle u^2\rangle\rangle^{1/2} = 0.12$ Å, and the complex inner potential was chosen as $V_0 = -(V_{0r} + iV_{0i})$, with $V_{0i} = 4$ eV and V_{0r} treated as an adjustable parameter in the course of the analysis, and fixed at 8 ± 2 eV at the end. The quality of the agreement between theoretical and experimental LEED spectra was assessed both visually and by means of r-factor calculations.[11]

Since the lattice parameter of the films in the planes parallel to the substrate surface was visibly established by the square net of the Pd{001} substrate, $a = 2.75$ Å, the analysis was aimed at the determination of three unknowns: the bulk interlayer spacing d_{bulk}, the first and the second interlayer spacing d_{12} and d_{23}. After a series of preliminary calculations, the refinement was made over the range $d_{\text{bulk}} = 1.518$, 1.568, 1.618, 1.668, and 1.718 Å, and for each of these values the change in d_{12} (Δd_{12}) was varied from -0.10 to $+0.10$ Å in steps of 0.05 Å, and the change in d_{23} (Δd_{23}) was varied between -0.20 and $+0.20$ Å in steps of 0.05 Å. For each calculation, an r-factor value was calculated with respect to the 6-layer-film data for V_{0r} varying from 0 to 10 eV in steps of 0.5 eV. This calculations with lowest r-factor values were also scrutinized visually to confirm acceptable fit to experiment. The best fit was produced by the following choices:

$$a = 2.75\ \text{Å}\,,$$

$$d_{\text{bulk}} = 1.62 \pm 0.03\ \text{Å}\,,$$

$$\Delta d_{12} = -0.05 \pm 0.03\ \text{Å}\,,$$

$$\Delta d_{23} = 0.00 \pm 0.03\ \text{Å}\,,$$

with $r = 0.12$. The calculated curves are compared to all three sets of experimental data in Fig. 1. Note that the 21 spectrum, which was not included in the refinement process, is also in good agreement with experiment. In general, the experimental peaks are markedly wider than the theoretical peaks, an indication of the presence of disorder in the films. This discrepancy could be reduced by the choice of a larger V_{0i}, which would widen the theoretical peaks and improve the agreement, but the change would be only cosmetic and would not affect the values of the structural parameters listed above.

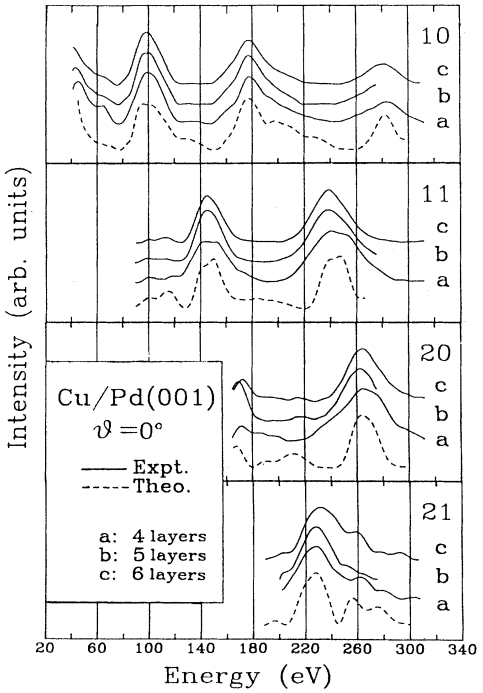

FIG. 1. Normal-incidence experimental (solid curves) and theoretical (dashed curves) 10, 11, 20, and 21 LEED spectra from 4-, 5-, and 6-layer films of Cu grown on clean Pd{001}.

Although the fit to experiment attained in Fig. 1 with calculations based on a semi-infinite Cu bulk is satisfactory, we also tested whether a calculation for a 4-layer Cu film on a semi-infinite Pd{001} substrate would improve the fit and possibly change the values of the structural parameters given above. This calculation produced curves similar to those dashed in Fig. 1, but with a higher best-fit r factor of 0.15 and a visibly worse fit to experiment. Thus, this test shows (1) that in the present case LEED is still somewhat sensitive to the 5th layer below the surface, and (2) that the better fit attained with the semi-infinite model suggests that the film thicknesses estimated from the AES data are too small, at least by 25% or 30%.

The conclusion of the LEED analysis is therefore that the bulk structural properties of the Cu films grown in this work were those of a bct phase with $c/a = 1.18$. A discussion of these results in connection with the predictions of first-principles calculations will be presented below, after the description of the ARPES experiments.

The electronic properties of the Cu films, in particular the valence bands, were studied with synchrotron radiation in the range from 14 to 165 eV at beam line U7 of the National Synchrotron Light Source. Experimental details and more extensive results will be reported elsewhere. Here we present only photoemission curves which confirm the novel character of the Cu phase grown in this work. Figure 2 depicts the evolution of the valence band in terms of angle-resolved electron-distribution curves (EDC's) measured at normal emission (NE) with 23-eV photons (25%-p-polarized) for increasing thickness of the Cu films. The bottom curve in the figure was measured on a clean Pd{001} surface, the top curve, on a clean fcc Cu{001} surface. The intervening curves were measured on the Pd substrate with Cu coverages (Θ) as indicated.

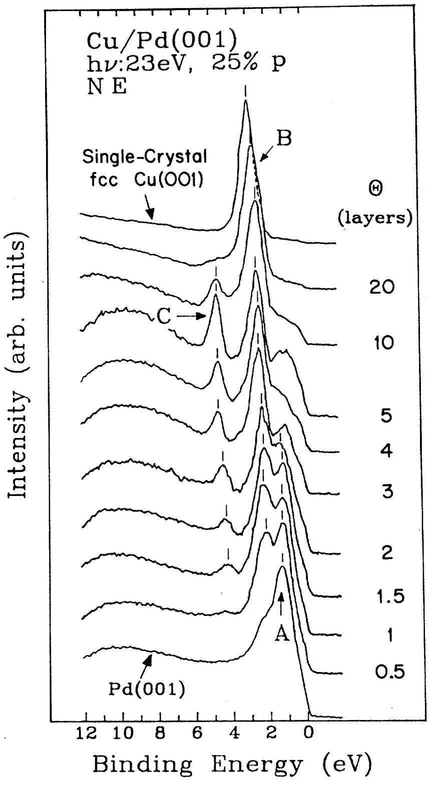

FIG. 2. Angle-resolved normal-emission photoemission curves from clean Pd{001} (bottom curve), clean fcc Cu{001} (top curve), and epitaxial Cu films with thickness values given on the right under Θ. The synchrotron light was 25%-p-polarized and the photon energy was 23 eV.

We note three main peaks, marked A, B, and C.

Peak A corresponds to emission from the Pd d band: with increasing thickness of the Cu film this peak decreases in intensity, but does not alter its energy position (1.35 eV below the Fermi level), indicating that there is no strong intermixing either at the interface or in the bulk of the films. Peak B is due to emission from the Cu d band. This peak appears already for $\frac{1}{2}$-monolayer coverage and its energy (2.13 eV at $\Theta = 0.5$) increases with coverage, reaching 2.75 for $\Theta = 20$, but never quite reaching the binding energy of the d band in fcc Cu (3.0 eV). Peak C does not exist in the EDC from fcc Cu, but is already present when the Cu film on Pd is a little thicker than 1 layer. Its energy also increases with Cu coverage, from 4.35 eV at $\Theta = 1$ to 4.80 eV at $\Theta = 5$, but then remains at 4.80 eV even when the Cu coverage is doubled. Figure 2 shows that the intensity of peak C reaches a maximum at $\Theta = 5$ (which corresponds to the coverage at which the LEED pattern still exhibits sharp diffraction beams on a medium background), but then decreases markedly to about $\frac{1}{3}$ of its maximum value at $\Theta = 10$ (when the LEED spots are broad and diffuse on a high background) and is practically invisible at $\Theta = 20$ (when no LEED pattern is visible). Peaks B and C appear to have the same dependence upon Cu coverage, as the binding-energy difference between the two is almost constant at 2.1 eV to within 0.1 eV. Peak C is sensitive to p polarization and is not visible in EDC's collected with s-polarized light. It has many attributes of a surface state in that it shows no dispersion with photon energy for normal emission and is sensitive to impurities coadsorbed on the surface. The sharp decrease in intensity at $\Theta = 20$ (Fig. 2) is also an indication of the sensitivity of peak C to the long-range order on the surface of the Cu film. We note that the binding energy of this state would lie in an energy gap of the electron band structure if the Cu films were fcc, but not if they were bcc.[10]

We conclude that the Cu grown on clean Pd{001} as described above is a new crystalline phase with both electronic and structural properties significantly different from those of the stable fcc modification. We now examine whether the bct films whose bulk structure has been determined by LEED might be a biaxially strained state of the fcc or bcc phases or of a true bct phase. If the structure of the films was strained fcc ($a_0 = 3.61$ Å), the misfit strain on Pd{001} ($a_0 = 3.89$ Å) would be 7.8% —very large for good epitaxy, hence very unlikely. If the structure of the films was strained bcc (theoretical $a_0 = 2.86$ Å from MKM), the misfit strain on Pd{001} ($a = 2.75$ Å) would be 3.8%, which is large for epitaxial growth of 10 layers, but possible. If the structure of the film was the new α-bct predicted theoretically by MKM ($a = 2.76$ Å), the misfit strain on Pd{001} would be very small (0.4%), and in fact perhaps too small for epitaxial growth of only 10 layers. We can compare with Fe on Cu{001} where a misfit strain of 0.6% permits growth of 20 layers. Clearly the most likely correct description of the structure of the film from the misfit augment is the α-bct phase, although the experimental mismatch appears to be greater than calculated. A plausible explanation of the observed larger mismatch is related to the fact that the theoretical lattice constant of bcc Cu is low. In fact, the augmented spherical wave (ASW) lattice constants of the $3d$ metals are known to be too low by up to 1.6% (Ref. 12)—although the error is rather less for Cu. If the bct Cu value $a = 2.76$ Å was increased by 1.6% to 2.79 Å (a value also quoted by MKM for the α-bct phase), the mismatch strain would increase to 2% and the observed thickness of 10 layers for the epitaxial films would be more reasonable.

However, this discussion of mismatch strain still leaves the possibility of a strained bcc phase. We now show that the observed phase was probably not bcc by an argument independent of MKM results. Under epitaxial strain, biaxial compression in the present case, the ratio of parallel strain $\delta a/a$ to perpendicular strain $\delta c/c$ is related to the Poisson ratio ν by[13]

$$\frac{\delta a/a}{-\delta c/c} = \frac{(a^{\text{meas}}-a)/a}{(c-c^{\text{meas}})/c} = \frac{1-\nu}{2\nu}, \qquad (1)$$

where $a^{\text{meas}} = 2.75$ Å, the side of the Pd{001} square mesh, and $c^{\text{meas}} = 2d_{\text{bulk}} = 3.24$ Å from the LEED analysis. Using the MKM value for bcc Cu of $c = a = 2.86$ Å in Eq. (1) we find $\nu = 0.63$, which is not physically possible (the shear modulus vanishes at $\nu = 0.5$). However, $a = 2.86$ Å is probably an underestimate, as noted above.[12] If we take $c = a = 2.87$ Å from ASW calculations[14] and use the maximum error found in the $3d$ metals of 1.6%, very probably high for Cu, then we find $a = c = 2.92$ Å and from (1) $\nu = 0.49$. This value of ν is barely possible, but very unlikely for bcc Cu, which is expected to have elastic properties close to fcc Cu ($\nu = 0.34$)—e.g., the bulk modulus of bcc Cu is close to that of fcc Cu, as can be seen from the similar $E(V)$ curves.[1,14]

This argument that the structure of the Cu films was probably not bcc is useful now because there is some uncertainty about the results of MKM. The $E(V)$ curve of these authors for bcc Cu shows features—a near double minimum—not found in other total-energy calculations on bcc Cu,[14,15] which could affect the total energy in the region of the bct phase and possibly give a spurious minimum. An ASW calculation of Moruzzi[16] does not yield the bct minimum, and hence shows that the existence of the bct minimum may depend on nonspherical parts of the charge and potential.

In summary, the present experiments have shown that bulk Cu films which were not fcc could be grown epitaxially on Pd{001}. A combination of measurements of bulk structure and of theoretical estimates of lattice constants suggests that the structure of the unstrained films was very probably not bcc. Hence the structure of the unstrained films was probably bct and was found to be close to a theoretical prediction of such a phase.

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[2] a is the side of the surface square, which is the cross section of the bct cell; $a = a_0/\sqrt{2}$ for the fcc lattice, where a_0 is the cubic lattice constant, and $a = a_0$ for the bcc lattice.

[3] The value of a for bcc Cu comes from the minimum of the smoothed curve in Fig. 3 of Ref. 1, which agrees with other theoretical calculations on bcc Cu, and not from the phase point given in Fig. 2 of Ref. 1 with $a = c = 2.82$ Å.

[4] These values correspond to the numerical minimum energy, point C in Fig. 5(a) of Ref. 1, rather than the phase point given in Fig. 2 of Ref. 1 at $a = 2.79$ Å, $c = 3.10$ Å. We think that the minimum-energy point corresponds to equilibrium, since the stresses in the transverse (a) direction and the perpendicular (c) direction vanish at the point.

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[13] Simply derived from the linear elastic equations for biaxial stress along cubic directions, see, e.g., A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover, New York, 1944), p. 103.

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