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Low-energy electron diffraction and photoemission study of epitaxial films of Cu on Ag{001}

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The epitaxy of Cu on Ag{001} is studied by qualitative and quantitative low-energy electron diffraction (LEED) and by angle-resolved photoemission. LEED indicates that ultrathin (two- to three-atomic-layer) films have a limited amount of long-range order, and the ordered component has interlayer spacings of 1.45±0.06 Å, which compares well with the theoretically determined cubic lattice constant 2.87±0.06 Å of a metastable body-centered-cubic (bcc) modification of Cu. Thicker (10- to 12-layer) films have almost no long-range order, and photoemission indicates that regions of bcc and fcc Cu coexist amid large amounts of defects.

I. INTRODUCTION

In the past few years a number of theoretical and experimental studies have been made of the presumed metastable body-centered-cubic (bcc) phase of Cu. Crystalline phases not normally found in nature are of considerable interest because they provide valuable tests of our understanding of crystal structure, and also present a challenge of experimental inventiveness to find ways of preparing and stabilizing them. There is special interest in studying Cu because in a number of ways Cu is the prototype metal for an accurate description by first-principles calculations; e.g., the face-centered-cubic (fcc) lattice constant is predicted correctly to within 0.3% by minimization of the total energy,[1] and the theory accounts well for the details of the photoemission spectrum.[2] A special reason for studying bcc Cu is that on the one hand calculations of total energy as a function of volume[1,3,4] exhibit a well-defined minimum at lattice constant $a_0=2.87$ Å (2.88 Å at 300 K) (Ref. 5) with only a small amount of metastability (between 0.3 and 3 mRy/atom). On the other hand, total-energy calculations on tetragonal distortions of Cu around the bcc structure indicate that the bcc structure is unstable.[6] Hence stabilization of the bcc lattice by pseudomorphic epitaxy is likely to be difficult and limited to very few atomic layers. In fact, an epitaxial film of Cu on fcc Pd {001} ($a_0=3.89$ Å, $a=2.75$ Å, Ref. 7) and on fcc Pt{001} ($a_0=3.93$ Å, $a=2.78$ Å, Ref. 8) is best described as having a strained fcc structure, although the mismatch strain of fcc Cu is larger in each case than that of bcc Cu (7.9% for fcc versus −4.5% for bcc on Pd{001}, 8.7% for fcc versus −3.5% for bcc on Pt{001}). For Cu on bcc Fe{001} ($a_0=2.87$ Å), the fcc and bcc strains are 12.1% and 0.3% and for Cu on fcc Ag{001} ($a_0=4.09$ Å, $a=2.89$ Å) they are 13.1% and 0.3% respectively. Hence both Fe{001} and Ag{001} are far more likely to stabilize the bcc Cu structure than Pd{001} and Pt{001}, as has been found experimentally.[9–13]

Bruce and Jaeger[9] were the first to report, in 1977, the epitaxial growth of thin films on Cu on a {001} surface of Ag. These authors used electron microscopy to examine Cu films grown at pressures ranging between 10^{-5} and 10^{-8} Torr, and found that films grown at 300 K and thinner than about 100 Å were pseudomorphic with the Ag{001} substrate and had bcc structure, while thicker films changed into {001} and {110} epitaxial fcc grains. A few years later, Smith, Norris, and Binns[10] concluded from the plot of Auger signals against evaporation time (at pressures of the order of 10^{-10} Torr) that the first atomic layer of Cu deposited on Ag{001} was pseudomorphic, and that the first, and possibly the second, atomic layer grew in the layer-by-layer mode. But films three layers thick and thicker were found to be no longer continuous.

Additional evidence for the existence of a bcc modification of Cu was provided in 1987 by Wang *et al.*[11] with a low-energy electron-diffraction (LEED) study of the growth of ultrathin films of Cu on an Fe{001} surface. The results of this study were ambiguous in the early stages of growth because LEED cannot distinguish between Cu and Fe if they have the same structure (in this case, the bcc structure). Thicker Cu films contained large amounts of defects and limited long-range order, but a small ordered component (about 20%) was shown to have a possibly somewhat distorted bcc structure. Later work by Egelhoff and Jacob[12] with reflection high-energy electron diffraction (RHEED) and x-ray-photoelectron forward scattering (XPS) found that Cu films grown on Ag{001} had bcc structure and showed that pronounced RHEED intensity oscillations could be observed during film growth at 77 K. This observation led the authors to the conclusion that the growth was "at least quasi-layer-by-layer" for at least five layers, the number of RHEED oscillations observed.

A new recent study, by Heinrich *et al.*,[13] confirmed the growth of bcc Cu on Fe{001} and identified the growth mode, again from RHEED oscillations, to be "good layer-by-layer" growth. This study argued that "the Cu{001} overlayers grow in a nearly perfect bcc structure" and deferred the determination of eventual "vertical distortions and surface relaxations of bcc Cu{001} grown on Fe{001}" to future LEED studies.

The LEED studies of the Cu/Fe system[11] were not able, in the early stages of growth, to exclude the presence of Fe atoms mixed with Cu atoms or the possibility of amorphous Cu layers, because Fe and Cu, as mentioned above, have about the same scattering properties for low-energy electrons. By contrast, LEED is expected to be able to distinguish well between Cu and Ag, which have very different ion cores. Furthermore, Wang *et al.*[11] have shown that their Cu films, grown on bulk Fe{001}, did not have the "nearly perfect bcc structure" of the Cu films that were grown by Heinrich *et al.*[11] on Fe{001} films grown, in turn, on bulk Ag{001}. It is therefore of interest to see whether Cu films grown directly on Ag{001} have in fact a nearly perfect bcc structure, and, if so, whether LEED can be used to determine the structural parameters of these films. Such is the purpose of the work described herein.

We give details of the experiments that we have carried out in Sec. II—the experimental tools were LEED, Auger-electron spectroscopy (AES), and synchrotron-based angle-resolved photoemission. We present the results in Sec. III and draw the conclusions of this work in Sec. IV.

II. EXPERIMENTS

The sample used in this study was a single-crystal Ag platelet with a major surface oriented perpendicular to a ⟨001⟩ direction to within 0.5° and mechanically polished to a mirror finish. The platelet was mounted on a three-axis sample manipulator[14] by means of Ta strips, and could be heated by electron bombardment of its back side. The temperature of the front surface was monitored with an infrared radiometer through a viewport in the experimental chamber.

The Ag{011} surface was cleaned *in situ* with several cycles of Ar-ion bombardments (ion energy varying between 400 and 600 eV) followed by annealing treatments at 600 °C for about 10 min. The chemical composition of the surface was monitored by AES with a cylindrical mirror analyzer (CMA): the only impurities present on the surface before the cleaning procedures were C and O, and their AES signals were reduced to below the noise level after the cleaning process.

The crystallinity of the surface was monitored with a reverse-view LEED system. The LEED pattern of the clean surface was a sharp and high-contrast 1×1 pattern. The diffracted intensities from the clean and the Cu-covered surfaces were measured with a computer-controlled video system.[15]

The Cu source was a small single crystal of Cu premelted on a W basket. The source was outgassed for several hours *in vacuo* so that deposition of Cu on the Ag{001} surface could be done at pressures lower than 4×10^{-10} Torr. The deposition rate was determined from the intensity ratio of the Cu AES signal at 918 eV to the Ag AES signal at 350 eV. Since there was no evidence, in this work, for layer-by-layer growth, we quote surface coverages not in numbers of layers, but in numbers of layer equivalents (LE), defined as the number of flat and complete layers than would produce the same ratio of AES Cu/Ag intensities as observed experimentally. The deposition rate used in the present experiments was typically about 1 LE per minute. The base pressure in the experimental chamber was in the low 10^{-11}-Torr range except during deposition of Cu.

The experiments were carried out at beamline U7B of the National Synchrotron Light Source in the Brookhaven National Laboratory. The photoemission experiments made use of a plane-grating monochromator, and the electron energies were analyzed with an angle-resolved double-pass CMA with an angular resolution of 2°. The combined energy resolution of monochromator plus analyzer was estimated to be 0.35 eV at $h\nu=100$ eV.

III. RESULTS AND ANALYSIS

A. LEED

The sharp, low-background 1×1 pattern typical of clean Ag{001} deteriorated very rapidly upon deposition of Cu: the diffraction beams broadened and the background increased markedly. The LEED pattern remained 1×1, as long as it was observable, for all coverages of the Ag{001} surface by Cu. Intensity-versus-voltage $[I(V)]$ spectra could be measured only in the initial stages, i.e., for surface coverages estimated to be lower than about 3–4 LE. At and above surface coverages of about 4–5 LE, the LEED pattern was practically obliterated, the diffracted beams being very broad and barely distinguishable above a high background. Prolonged deposition of Cu, up to 10–15 LE, did not improve or change the LEED pattern in any noticeable way.

We show in Fig. 1 the 10, 11, and 20 $I(V)$ spectra from a Cu film estimated to be 2–3 LE thick (Cu-to-Ag AES ratio of 0.19) for normal incidence of the primary electron beam. The curves marked "raw" are the $I(V)$ spectra as collected—they are shown here to demonstrate how large the background and how small the signal-to-background ratio was at this surface coverage.

In order to use these $I(V)$ spectra for quantitative analysis of the Cu film, we had to normalize the curves to constant incident-electron current and to subtract the background—an operation of considerable uncertainty in the present case. The $I(V)$ spectra obtained after this operation are marked "Expt." in Fig. 1. It is obvious that only the positions of the major intensity peaks, not the details of the curves, can be trusted. Nevertheless, we tried to fit these curves with $I(V)$ spectra calculated for different models of the Cu film.

The intensity calculations were done with the CHANGE computer program.[16] The Cu and Ag potentials were taken from the compilation of Moruzzi, Janak, and Williams,[17] eight phase shifts and 61 beams were used, the inner potential was chosen to be $V_0=-(10+4i)$ eV, and the amplitude of atomic vibrations was set at $\langle u^2\rangle^{1/2}=0.156$ Å for both Cu and Ag.

Since the coverage was not precisely known, several models of the Cu film were tried, viz., one, two, three, and four pseudomorphic layers of Cu on Ag{001}, and a semi-infinite film of Cu with an in-plane lattice constant equal to that of Ag{001} (2.889 Å) and interlayer spacing varying between 1.3 and 1.6 Å in intervals of 0.05 Å. Evaluation of the fit to experiment was done both visually and by R factor [R_{VHT},[18] R_{P},[19] and r_{ZJ} (Ref. 20)]. The best fit was found with models involving two and three layers of Cu. Figure 1 depicts 10, 11, and 20 spectra calculated for two layers of Cu (curves marked "2") with interlayer distances $d_{\text{Cu-Cu}}=1.45$ Å and $d_{\text{Cu-Ag}}=1.52$ Å ($R_{\text{VHT}}=0.45$, $R_{\text{P}}=0.72$, $r_{\text{ZJ}}=0.25$), and for three layers of Cu (curves marked "3") with interlayer distances $d_{\text{Cu-Cu}}=1.50$ Å and $d_{\text{Cu-Ag}}=1.4$ Å ($R_{\text{VHT}}=0.59$, $R_{\text{P}}=0.68$, $r_{\text{ZJ}}=0.40$). The agreement between theory and experiment is not as good as in a high-quality structure determination, owing to the meager and rather uncertain raw experimental data, and because the Cu film was very probably of uneven thickness, with regions two, three, and four layers thick present at the same time. However, the agreement is acceptable to permit some significant structural information to be obtained.

Thus, our LEED experiment indicates that the Cu films grown on Ag{001} were full of defects and disorder, and that even poor-quality LEED patterns could only be observed for thicknesses up to 3–4 LE, but that the ordered regions of the films involved Cu-Cu and Cu-Ag interlayer spacings of 1.45±0.06 Å.

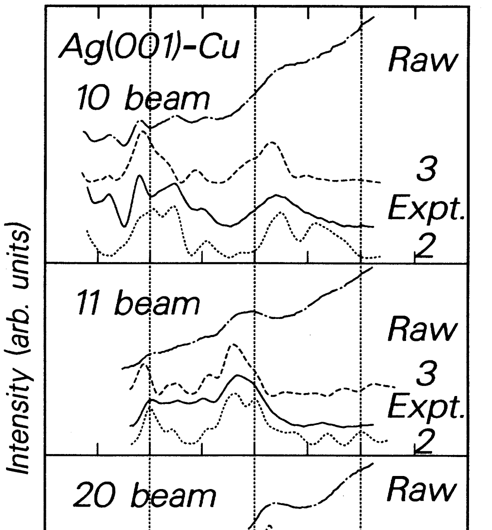

FIG. 1. Experimental and theoretical LEED $I(V)$ spectra for ultrathin films of Cu on Ag{001}. "Raw" denotes curves as measured; "Expt." denotes the same curves after normalization to constant incident-electron current and subtraction of the background; "2" and "3" denote calculated curves for 2 and 3 layers of Cu on Ag{001}, respectively, with interlayer distances given in the text.

B. Photoemission

The photoemission experiments involved a collection of angle-resolved electron-distribution curves (EDC's) for emission normal to the film surface, for photon energies ranging from 13 to 160 eV, and for surface coverages ranging from 0 to 10 LE. We show in Fig. 2 a series of EDC's measured with s-polarized light on a Cu film estimated to be about 10 LE thick (the corresponding LEED pattern was essentially obliterated by high background). The features located deeper than about 4 eV below the Fermi level E_F are due to the underlying Ag{001} substrate; those at higher binding energies stem from the Cu film.

Comparison of Fig. 2 with equivalent plots for bulk fcc Cu{001} (Refs. 21–23) shows obvious differences. For example, in fcc Cu, the EDC's for $h\nu=100$ eV exhibit two well-resolved peaks in the range between 2 and 6 eV below E_F, whereas the present data have only a peak with a broad tail on the higher-binding-energy side. Furthermore, in Fig. 2 the extrema in binding energy occur approximately for 50- and 130-eV photons (while in fcc Cu{001} they occur at 40 and 95 eV, respectively). If we evaluate the corresponding momentum values by assum-

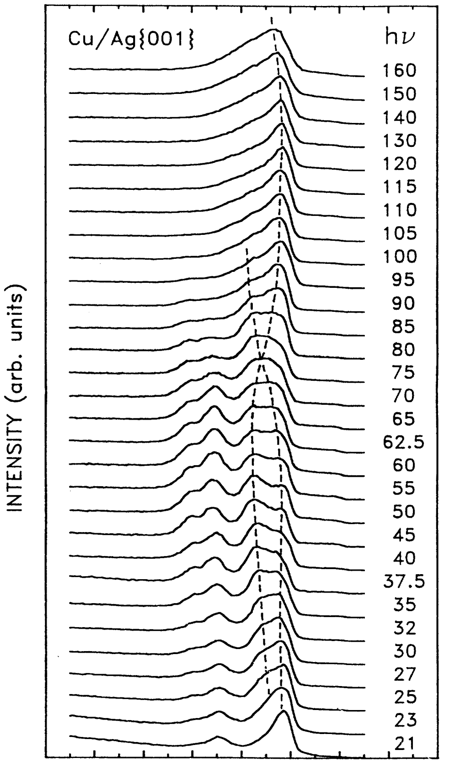

FIG. 2. Normal-emission angle-resolved electron-distribution curves from a 10-layer Cu film on Ag{001} for s-polarized light and photon energies between 21 and 160 eV. The features below −4 eV are due to the Ag substrate. The dotted lines outline a possible crossing of the corresponding bands.

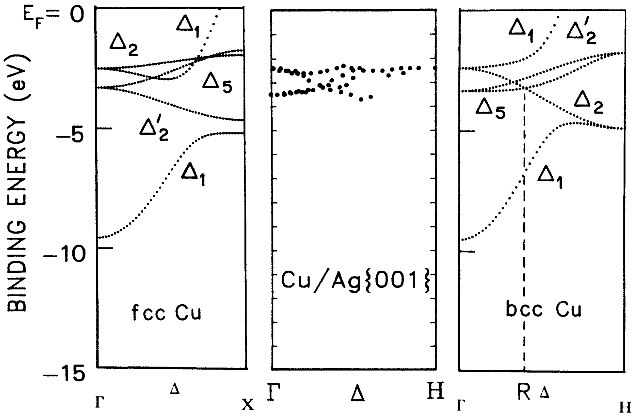

FIG. 3. Calculated electron band structure [after Moruzzi (Ref. 25)] for fcc Cu (left) and bcc Cu (right), and experimental band structure (center) determined with *s*-polarized data from films of Cu on Ag{001} in the free-electron approximation.

ing as valid the free-electron parabolic relation

$$k_{f\perp}=0.512\sqrt{h\nu+E_F-E_b} \qquad (1)$$

($k_{f\perp}$=final-state momentum perpendicular to the surface inside the crystal, in Å^{-1}; $h\nu$=photon energy, in eV; E_F=Fermi energy, in eV, with respect to the bottom of the band; E_b=positive binding energy below E_F, in eV), we find, with $E_F=4$ eV and $E_b=2.5$ eV (Ref. 24), that $k_{f\perp}=3.69$ Å^{-1} and $k_{f\perp}=5.88$ Å^{-1}, respectively. The difference between these values is 2.19 Å^{-1}, which should correspond to the length of the Brillouin zone in the direction normal to the film surface. If the film had bcc structure, this length would be the distance between the Γ and the *H* points. Thus, from $\Gamma H=2.19$ Å^{-1} we calculate an interlayer distance of 2.87 Å. The fact that this result agrees so well with the theoretical value of the lattice constant of bcc Cu may be accidental, but it does support the existence of a bcc structure.

Additional evidence for a component with bcc structure comes from the trend of the experimental EDC's shown in Fig. 2 compared to the calculated band structure of bcc Cu,[25] which is reproduced on the right-hand side of Fig. 3. This figure shows that the Δ_2 and the Δ_5 bands cross each other at the point marked *R*, and such a crossing seems indeed to occur in the experiment as indicated by the dashed lines in Fig. 2. However, there is also evidence for the presence of a fcc component. In fact, evaluation of the electron band structure under the free-electron assumption of Eq. (1) produced the data points presented in the center of Fig. 3. Comparison with the calculated band structure of fcc Cu (left-hand side of Fig. 3) shows that a characteristic unique to the fcc band structure, the quasihorizontal Δ_2 band, is reproduced in the experimental data, while a characteristic unique to the bcc band structure, the downward-sloped Δ_2 band, is also reproduced in the experiment (recall that the Δ_1 band is not visible in these *s*-polarized data). Thus, the data suggest that both bcc and fcc regions coexisted in the film investigated amidst a large amount of defects.

IV. CONCLUSIONS

The combined LEED and photoemission experiments described above allow the conclusion that the ultrathin Cu films grown on clean Ag{001} in this work had a crystalline component with bcc structure, the interlayer spacing along ⟨001⟩ being 1.45±0.06 Å. But the films contained a large amount of defects, steps, and disordered regions, which manifested themselves in broad diffracted beams and high background of the LEED pattern. In fact, films thicker than about 3 or 4 layers were predominantly disordered and had little or no long-range order. Photoemission indicated that 10-layer films contained regions with bcc and fcc structure.

Thus, with regard to the bcc modification of Cu, the present results confirm the conclusions reached by Wang *et al.*[11] in their study of the growth of Cu on Fe{001}, but do not confirm the near perfection of the bcc structure and the layer-by-layer growth mode of the Cu films that is suggested by the RHEED patterns and RHEED oscillations as published in the literature.[12,13] We offer three possible explanations for this contradiction, as follows. (i) Both the presence or absence of long-range order and the mode of growth of the epitaxial films may depend on the nature and the quality of the substrate surfaces, on the deposition rate, and in general on the details of the procedures used in different experiments in different laboratories. (ii) The growth mode may indeed be layer by layer even though the long-range order is limited or absent. (iii) The growth mode may not be layer by layer, and perhaps RHEED oscillations could be observed even when the long-range order is limited and the growth is *not* layer by layer.

ACKNOWLEDGMENTS

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[1] P. M. Marcus, V. L. Moruzzi, Z. Q. Wang, Y. S. Li, and F. Jona, in *Physical and Chemical Properties of Thin Metal Overlayers and Alloy Surfaces,* Vol. 83 of *Materials Research Society Proceedings,* edited by D. M. Zehner and D. W. Goodman (MRS, Pittsburgh, 1987), p. 21.

[2] See, e.g., V. L. Moruzzi, P. M. Marcus, and J. A. Knapp, in *Transition Metals 1977,* Inst. Phys. Conf. Ser. No. 39, edited by M. J. G. Lee, J. M. Perz, and E. Fawcett (IOP, Bristol, 1977), p. 234; D. W. Jepsen, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B **36**, 4039 (1982).

[3] J. R. Chelikowsky and M. Y. Chou, Phys. Rev. B **38**, 7966 (1988).

[4] Z. W. Lu, S.-H. Wei, and A. Zunger, Phys. Rev. B **41**, 2699 (1990).

[5] This result is obtained if the value of the equilibrium bcc lattice constant for the rigid lattice is corrected to 300 K by the same fractional amount as the known fcc lattice constant.

[6] Private communication from H. Jansen; the shear constant $G=(c_{11}-c_{12})/2$ is negative and the lattice is unstable with respect to $\langle 110 \rangle$ shears.

[7] H. Li, S. C. Wu, D. Tian, J. Quinn, Y. S. Li, F. Jona, and P. M. Marcus, Phys. Rev. B **40**, 5841 (1989). The cubic lattice constant is designated a_0, and the side of the primitive square mesh on the fcc$\{001\}$ surface is labeled a.

[8] Y. S. Li, J. Quinn, H. Li, D. Tian, F. Jona, and P. M. Marcus (unpublished).

[9] L. A. Bruce and H. Jaeger, Philos. Mag. **36**, 1331 (1977).

[10] G. C. Smith, C. Norris, and C. Binns, J. Phys. C **17**, 4389 (1984).

[11] Z. Q. Wang, S. H. Lu, Y. S. Li, F. Jona, and P. M. Marcus, Phys. Rev. B **35**, 9322 (1987).

[12] W. F. Egelhoff, Jr. and I. Jacob, Phys. Rev. Lett. **62**, 921 (1989).

[13] B. Heinrich, Z. Celinski, J. F. Cochran, W. B. Muir, J. Rudd, Q. M. Zhong, A. S. Arrott, K. Myrtle, and J. Kirschner, Phys. Rev. Lett. **64**, 673 (1990).

[14] Y. Dai, H. Li, and F. Jona, Rev. Sci. Instrum. **61**, 1724 (1990).

[15] F. Jona, J. A. Strozier, Jr., and P. M. Marcus, in *The Structure of Surfaces*, edited by M. A. Van Hove and S. Y. Tong (Springer, Berlin, 1985), p. 92.

[16] D. W. Jepsen, Phys. Rev. B **22**, 814 (1980); **22**, 5701 (1980).

[17] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculations of Electronic Properties of Metals* (Pergamon, New York, 1978).

[18] M. A. Van Hove, S. Y. Tong, and M. H. Elconin, Surf. Sci. **64**, 85 (1977).

[19] J. B. Pendry, J. Phys. C **13**, 937 (1980).

[20] E. Zanazzi and F. Jona, Surf. Sci. **62**, 61 (1977).

[21] J. A. Knapp, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B **19**, 4952 (1979).

[22] S. C. Wu, J. Sokolov, C. K. C. Lok, J. Quinn, Y. S. Li, D. Tian, and F. Jona, Phys. Rev. B **39**, 12 891 (1989).

[23] S. C. Wu, C. K. C. Lok, J. Quinn, Y. S. Li, D. Tian, and F. Jona, Phys. Rev. B **39**, 13 218 (1989).

[24] H. Li, S. C. Wu, D. Tian, J. Quinn, Y. S. Li, F. Jona, and P. M. Marcus, in *The Structure of Surfaces III*, edited by S. Y. Tong and M. A. Van Hove (Springer-Verlag, New York, 1991).

[25] V. L. Moruzzi (private communication).