RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 17 15 JUNE 1987-I

Epitaxial growth of a metastable modification of copper with body-centered-cubic structure

Z. Q. Wang,* S. H. Lu,* Y. S. Li, and F. Jona
College of Engineering and Applied Sciences, State University of New York at Stony Brook, Stony Brook, New York 11794

P. M. Marcus
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 3 March 1987)

Slow deposition of Cu onto a clean unheated Fe{001} surface produced films with large amounts of defects, but still detectable crystallinity. Low-energy electron diffraction showed that the films contained regions with a (somewhat distorted) body-centered-cubic structure and the same or nearly the same lattice parameter as the underlying substrate. Auger-electron spectroscopy suggested that the crystalline regions were essentially pure Cu, thus allowing the conclusion that a metastable bcc modification of Cu has been realized, consistent with the predictions of total-energy band calculations reported elsewhere.

Total-energy spin-polarized band calculations carried out for a series of values of volume and (for magnetic elements) magnetic moment per atom have provided good estimates of equilibrium, i.e., zero-pressure lattice constants of metallic elements.[1,2] Results were obtained not only for standard bulk phases, but also for metastable phases not ordinarily found in bulk. Thus, the theory predicts that Cu may form a metastable body-centered-cubic (bcc) phase with a cubic-cell lattice constant of 2.87 Å for a rigid lattice (i.e., without zero-point or thermal motion) and with cohesive energy only slightly smaller in magnitude than that of the stable face-centered-cubic (fcc) Cu phase. The theory also predicts a value of 2.82 Å for the lattice constant of the stable bcc phase of Fe in a rigid lattice (the experimental value[3] at 20 °C is 2.866 Å, part of the difference from the rigid-lattice value, possibly one-half of it, being due to zero-point and thermal expansion). If we compare the two rigid-lattice results we expect bcc Cu to grow readily in a strained epitaxial film on bcc Fe, since the strain is small (1.8% compression of the Cu lattice) and the cohesive-energy difference between the metastable and stable phase is small. At finite temperature the strain will probably be reduced, since both Cu and Fe will expand and Cu (in the fcc modification) has a larger coefficient of thermal expansion than Fe.

Such realizations of metastable phases through the growth of epitaxial thin films on suitable substrates have been reported as successful in the recent literature, viz., bcc Co on GaAs,[4] fcc Fe on Cu,[5-8] and bcc Ni on Fe.[9,10] It is of interest to compare the epitaxial pairing of metastable bcc Cu on a substrate of stable bcc Fe with the inverse pairing of metastable fcc Fe on a substrate of stable fcc Cu, which readily produces epitaxial films of fcc Fe.[5-8] The equilibrium lattice constants of the rigid lattices are 3.44 Å for (nonmagnetic) Fe and 3.61 Å for Cu,[2] which would correspond to a 4.9% stretch of the Fe lattice when deposited on Cu. However, the ferromagnetic phase of fcc Fe becomes more stable at 3.62 Å and is much less strained, and hence should be the preferred phase.

We describe below a series of experiments aimed at growing bcc Cu films on a clean Fe{001} substrate. The experiments were done in an ultrahigh-vacuum chamber with low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES) facilities. Cleaning of the substrate was done *in situ* with a series of Ar-ion bombardments (5×10^{-5} Torr, 500 eV, 1.3 $\mu A/cm^2$) lasting from 2 to 15 h and followed by 10-min anneals at 500 °C. AES spectra of the final product revealed no recognizable impurities except traces of C [see Fig. 1(a)]. The LEED pattern of the annealed surface featured sharp spots on low background, indicative of good long-range order.

The Cu source was a small single crystal of Cu wrapped in Ta foil and located about 10 cm away from the Fe substrate, which was not intentionally heated during deposition. In the experiments described below the source was heated to approximately 800 °C to provide a deposition rate of about 1 monolayer/3 min. This rate was determined by monitoring the decrease in intensity of the (doubly differentiated) AES peak of Fe at 703 eV. The inset in Fig. 1 depicts the decrease of the Fe signal at 703 eV and the increase of the Cu signal at 920 eV with increasing deposition. The thickness of the deposited film was calculated by assuming that the Fe signal was reduced by absorption of the Auger electrons in a pure Cu film. The formula used was $I=I_0\exp(-d/0.8\lambda)$, where I and I_0 are the intensities of the 703-eV Fe signal measured after and before deposition of Cu, respectively; d is the unknown thickness of the deposited film and λ is the mean free path of 703-eV electrons in Cu ($\lambda=12.7$ Å, according to Ashley and Tung[11]). The factor 0.8 represents a correction required by the finite solid angle for the Auger-electron collection of the LEED optics.[12] The conversion of thickness d from angstrom units to number of layers was done with the relation (assuming bcc Cu) 1.4 Å = 1 monolayer. We see in the inset in Fig. 1 that the Fe AES signal is still detectable, albeit strongly reduced, through a Cu film with a nominal thickness of 12 layers.[13] Only after deposition of 25 to 30 Cu layers did the Fe signal disappear in

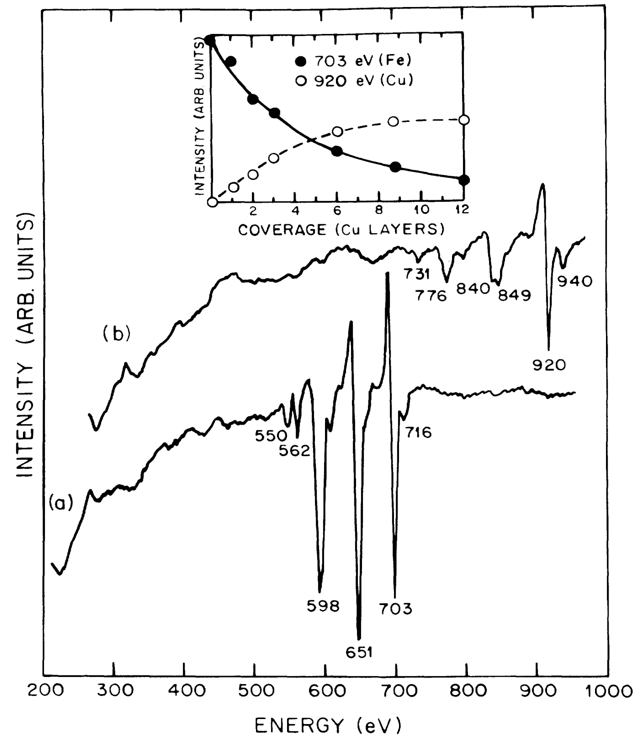

FIG. 1. AES spectra from (a) clean Fe{001}, showing only Fe lines at 550, 562, 598, 651, 703, and 716 eV; (b) Cu film about 25 layers thick on top of the Fe substrate (the Fe signal is obliterated and only Cu lines at 731, 776, 840, 849, 920, and 940 eV are visible). Inset: Decrease of the 703-eV Fe line and increase of the 920-eV Cu line vs coverage in number of Cu layers.

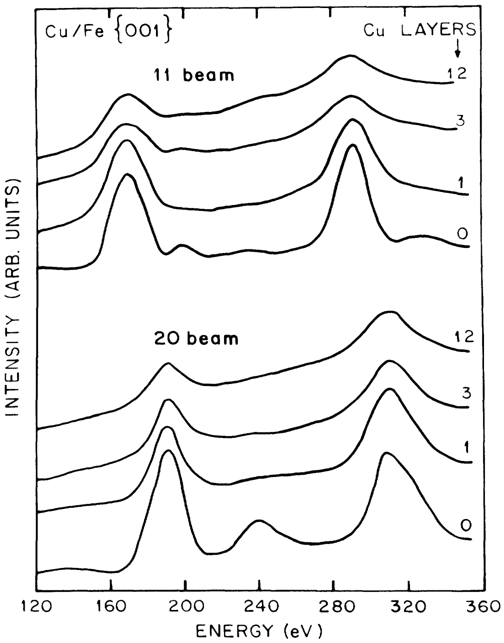

FIG. 2. Effect of Cu deposition on the 11- and the 20-beam LEED spectra. The numbers on the right indicate the number of Cu layers deposited—0 refers to the clean Fe{001} surface.

the noise. We note in Fig. 1(b) that when the Cu film was so thick as to obliterate the Fe signal the 920-eV Cu line was about half as strong as the 703-eV Fe line from the original clean substrate surface.

The LEED observations were as follows. The deposition of Cu onto the clean Fe{001} deteriorated the LEED pattern in the sense that the diffracted beam intensities decreased and the background appeared to increase, but the geometry remained 1×1. Only after deposition of rather thick films (25–30 Cu layers) did we observe a few broad non-integral-order beams, but the integral-order spots were still present, albeit barely visible above a large background. The energy dependence of the diffracted intensities remained fundamentally unaltered, except for increased broadening of the major peaks and enhanced kinematic character of the spectra. Figure 2 shows the 11- and the 20-beam LEED spectra for clean Fe{001} and for coverages of 1, 3, and 12 Cu layers. It is obvious that with increasing surface coverage the major peaks (which are the kinematic, or Bragg, peaks) persist, although their intensities decrease and their full widths at half maximum increase, and that the minor peaks (which are dynamical, or multiple-scattering, peaks) are almost abruptly extinguished.

Figure 3 shows quantitatively the decay of the integrated intensity of the 20 beam (with background subtracted) at 190 and at 310 eV (two Bragg peaks). The solid curves were calculated under the assumption that the deposited Cu film may be amorphous, so that both the incident and the diffracted beam would be damped upon crossing the film, and the diffraction pattern would be due solely to the underlying Fe{001} surface. The experimental data in Fig. 3 indicate that this assumption is not wholly correct. Indeed, the rapid decay and the attendant broadening of the diffracted peaks point toward the existence of defects and strains or, in general, disorder in the deposited films, but the persistence of the diffracted peaks themselves shows that about 20% of the surface had substantial long-range order corresponding to a bcc structure.

The question of interest concerns the nature of this 20% ordered contribution to the LEED pattern. Three possible sources of this contribution come to mind: (1) bare regions of the underlying Fe{001} surface, (2) islands of bcc Cu{001}, and (3) islands of bcc Cu-Fe alloys formed by interdiffusion during film growth.

We argue that hypothesis (1) is improbable. This hypothesis would require the persistence of relatively large bare patches of Fe surface even when the surrounding islands of disordered Cu have grown to be about 15 layers thick—an improbable situation. Moreover, at a coverage of about 12 layers of Cu the Fe AES signal is still decreasing with coverage (Fig. 1), while the LEED signal has leveled off (Fig. 3), and at a coverage of about 25 layers of Cu the Fe AES signal has disappeared (Fig. 1), while the LEED signal persists, although very weakly (see above).

Hypothesis (2) requires the existence of a bcc modification of Cu with the same or nearly the same lattice parameter as bcc Fe, and requires also (because of re-

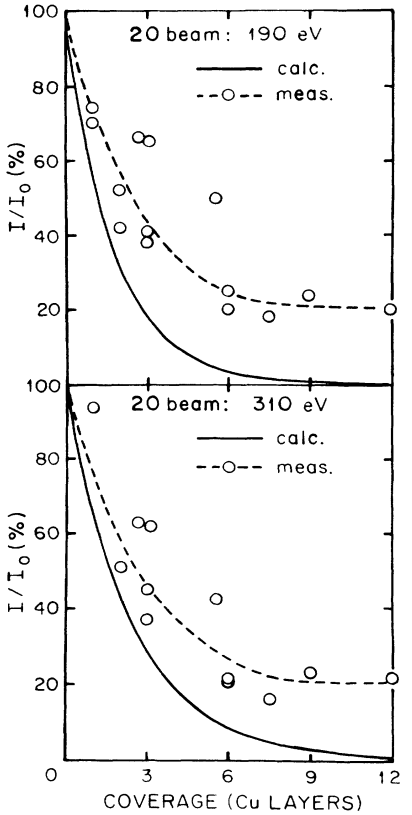

FIG. 3. Decay of the intensity of the 20 beam at 190 and 310 eV upon deposition of Cu onto clean Fe{001} (see text).

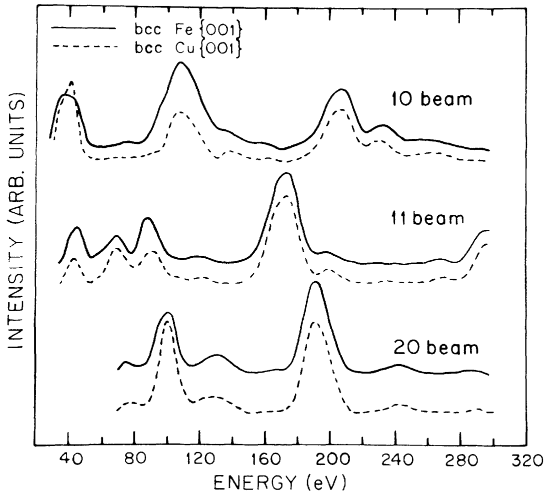

FIG. 4. Calculated 10-, 11-, and 20-beam LEED spectra from bcc Fe{001} and bcc Cu{001} with the same lattice constant.

sults such as Fig. 2) a close similarity between the LEED spectra produced by bcc Cu{001} and that produced by bcc Fe{001}. The first requirement is probably met, as suggested by the results of the total-energy band calculations mentioned above.[1,2] The second requirement is also met, as demonstrated by the curves in Fig. 4. The figure depicts the 10-, 11-, and 20-beam LEED spectra as calculated for bcc Fe{001} and for isomorphous bcc Cu{001} with the same lattice constant. It is obvious, as observed repeatedly before,[2,14] for other similar cases, that LEED cannot easily distinguish between elements with nearly the same atomic numbers, such as Cu and Fe, if they have the same structure. Thus, hypothesis (2) is possible and probable.

We also argue that hypothesis (3) is improbable. Fe-Cu alloys with the bcc structure and with lattice parameters varying from 2.866 Å for pure Fe to 2.91 Å for 50% Fe–50% Cu have been prepared.[15,16] These alloys are unstable and decompose, upon heating to 300°–600°C, into nearly pure bcc Fe and nearly pure fcc Cu.[15] At room temperature, only the alloys with less than 50% Cu have the bcc structure, while alloys with more than 70 at.% Cu have the fcc structure and alloys with Cu content between 50 and 70 at.% could not be prepared.[15] The latter results make hypothesis (3) rather improbable. If the LEED pattern from, say, a 12-layer-thick Cu film (see Fig. 2) were due to a bcc Cu-Fe alloy, then the Cu content of that film would have to be *at most* 50%. But the AES results from pure Fe and pure Cu would predict (see the discussion above) that a 50%-Cu–50%-Fe film should produce simultaneously a 703-eV Fe signal and a 920-eV Cu signal, the former about twice as large as the latter, which was not the case (see inset in Fig. 1).

We therefore conclude that the ordered portions of the films grown in this work were probably made of bcc Cu with the lattice parameter equal or almost equal to that of bcc Fe (2.866 Å). The quick extinction of multiple scattering peaks in the LEED spectra, and the consequent kinematic character of the same (Fig. 2), seem to indicate, however, that the long-range order was not very good. The extinction of multiple-scattering peaks in the LEED spectra of a substrate upon deposition of foreign atoms has been observed before[17] and, although not thoroughly understood, has been ascribed to distortions of the host lattice.

In conclusion, we believe that the work described above has been partially successful in producing the metastable bcc modification of Cu that was predicted by total-energy band structure calculations.[1] The Cu films grown on Fe{001} were largely disordered, but a small ordered component (20% or less) consisted of a somewhat distorted bcc structure of Cu.

This work was sponsored in part by the National Science Foundation under Grant No. DMR8301165A01.

*Permanent address: Physics Department, Peking University, Beijing, People's Republic of China.

[1] V. L. Moruzzi, P. M. Marcus, K. Schwarz, and P. Mohn, Phys. Rev. B **34**, 1784 (1986).

[2] 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,* Materials Research Society Symposia Proceedings, Vol. 83, edited by D. M. Zehner and D. W. Goodman (Materials Research Society, Pittsburgh, PA, 1987).

[3] A. Taylor and Brenda J. Kagle, *Crystallographic Data on Metal and Alloy Structures* (Dover, New York, 1963).

[4] G. A. Prinz, Phys. Rev. Lett. **54**, 1051 (1985).

[5] J. G. Wright, Philos. Mag. **24**, 217 (1971).

[6] W. Kummerle and U. Gradmann, Solid State Commun. **24**, 33 (1977); U. Gradman and P. Tillmanns, Phys. Status Solidi (a) **44**, 539 (1977).

[7] W. Keune, R. Holbauer, U. Gonser, J. Lauer, and D. L. Williamson, J. Appl. Phys. **48**, 2976 (1977).

[8] P. A. Montano, Y. C. Lee, J. Marcano, and H. Min, in *Layered Structures and Epitaxy,* Materials Research Society Symposia Proceedings, Vol. 56, edited by J. M. Gibson, G. C. Osbourn, and R. M. Tromp (Materials Research Society, Pittsburgh, PA, 1986), p. 183.

[9] B. Heinrich, A. S. Arrott, J. F. Cochran, C. Liu, and K. Myrtle, J. Vac. Sci. Technol. **4**, 1376 (1986).

[10] Z. Q. Wang, Y. S. Li, F. Jona, and P. M. Marcus, Solid State Commun. **61**, 623 (1987).

[11] J. C. Ashley and C. J. Tung, Surf. Interface Anal. **4**, 55 (1982).

[12] M. P. Seah, Surf. Sci. **32**, 703 (1972).

[13] The uncertainties in the data presented in the inset of Fig. 1 are estimated as follows. The intensities are tagged with an error of about 10%, which corresponds approximately to the diameter of the circles drawn to show the data points in the figure. The surface coverage in terms of Cu layers has a systematic uncertainty estimated to be about 50%, almost entirely due to the uncertainty in the electron mean free path. The exponential formula $I = I_0 \exp(-d/0.8\lambda)$ was used to estimate the thickness of *thick* films (25–30 layers), thereby calibrating the *rate* of deposition. The thickness of very thin films was then estimated from the deposition time at the constant rate determined before. We note, however, that the arguments presented below about the growth of Cu films do not depend on the precise quantitative value of the electron mean free path, but rather on the qualitative conclusion of the disappearance of the Fe signal upon deposition of Cu.

[14] F. Jona, J. Phys. C **11**, 4271 (1978).

[15] E. F. Kneller, J. Appl. Phys. **35**, 2210 (1964).

[16] W. Klement, Jr., Trans. Metall. Soc. AIME **233**, 1180 (1965).

[17] W. S. Yang, S. C. Wu, and R. G. Zhao, Phys. Rev. B **33**, 919 (1986).