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Hexagonal close-packed copper: Theory and experiment

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First-principles total-energy calculations on the hexagonal close-packed (hcp) states of bulk elemental copper have been made with a full-potential electronic-structure program within both the local-density approximation and the generalized gradient approximation. The epitaxial Bain path shows the existence of two energy minima for hcp states with axial ratios $c/a=0.68$ and 1.69. For both states and for both approximations the shear elastic constants c_{44} are found to be negative, proving that both states are unstable in bulk. Experiments using vacuum deposition of Cu on a W {001} surface reveal the presence of a weak $c(2\times2)$ pattern, even in films thicker than 20 Å. A low-energy electron diffraction analysis shows that this pattern is due to a strained $(11\bar{2}0)$ film in pseudomorphic epitaxy of the hcp phase with $c/a=1.69$, which is stabilized by pseudomorphic epitaxy in small regions, even in surprisingly thick films.

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I. INTRODUCTION

In 1996, Wormeester, Hüger, and Bauer (WHB) reported the growth of hexagonal close-packed (hcp) Cu in the form of $(11\bar{2}0)$-oriented epitaxial thin films on W{001}.[1] Diffracted beams at $(\frac{1}{2}, \frac{1}{2})$ positions in reflection-high-energy-electron-diffraction spectra indicated a $c(2\times2)$ structure with respect to the square-net substrate. There is a previous example of a hcp$(11\bar{2}0)$ film producing a $c(2\times2)$ net on a square substrate, namely, Co$(11\bar{2}0)$ on FeAl{001} grown pseudomorphically,[2] but in that case the grown phase was the ground state. The unit mesh of hcp$(11\bar{2}0)$ is rectangular with the two edges oriented along the $[1\bar{1}00]$ and [0001] directions. In the present case WHB observed different transmission patterns along those directions, proving that the grown films were *not* pseudomorphic to the substrate. The lattice parameters of hcp Cu were then not known—the misfit to the W{001} substrate was estimated from the ratio of the atomic radii of the film and substrate atoms. It was also not known whether hcp Cu is a metastable or an unstable phase. But in either case it is surprising to see that such a non-ground-state phase would grow unconstrained, i.e., nonpseudomorphically, even if epitaxially, on a square-net substrate.

The WHB observations stimulated us to ask: (a) whether an hcp Cu phase exists at all; (b) if it exists, whether the phase is metastable or unstable; and (c) whether we could reproduce WHB's experiment and identify the phase grown in the experiment. We report here the answers to those questions: (a) and (b) by means of total-energy calculations (in Sec. II), and (c) by low-energy electron diffraction (LEED) observations and quantitative intensity analysis (in Sec. III).

II. CALCULATIONS AND RESULTS

The total-energy calculations were done with the WIEN97 program developed by Blaha and coworkers.[3] This program uses the full-potential linearized augmented plane wave method to calculate total energies for a variety of crystal structures and space groups with a choice of nonrelativistic (NREL) or relativistic (RELA) calculations in either the local-density approximation (LDA) or the generalized gradient approximation (GGA). The calculations discussed in this paper were done both with the NREL-LDA and with the RELA-GGA formulation. In both cases we used a large plane-wave cutoff of $R_{\mathrm{mt}}K_{\max}=9$, where R_{mt} is the muffin-tin radius, corresponding to about 1200 plane waves; a muffin-tin radius $R_{\mathrm{mt}}=2.0$ bohr for the Cu atom, a magnitude $G_{\max}=14\ \mathrm{bohr}^{-1}$ for the largest vector in the charge-density Fourier expansion; a criterion of 1×10^{-6} Ry for energy convergence; and 8000 k points in the full Brillouin zone (BZ) for 450 k points in the irreducible wedge of the BZ.

The procedures followed for the calculation of an epitaxial Bain path (EBP) have been described elsewhere for hexagonal structures.[4] The hcp unit cells considered here are described by the edge a of the primitive rhombus base with angle $\gamma=120°$ (or 60° for calculations of the c_{44} elastic constant) and the height c.

Figure 1 depicts the results in the form of relative energy/atom $E-E_0$ versus axial ratio c/a (top panel) and normalized volume per atom V/V_0 versus c/a (bottom panel). E_0 is the smallest energy value found ($E_0=-3259.046\,750$ Ry for the LDA and $E_0=-3292.602\,518$ Ry for the GGA); V_0 is the volume/atom of the high c/a phase ($V_0=18.95\ \text{Å}^3$ for the LDA and $V_0=20.98\ \text{Å}^3$ for the GGA). Two energy minima are found, one at low c/a (0.676 for LDA, 0.678 for GGA), another at high c/a (1.695 for LDA, 1.685 for GGA). With LDA the lowest energy state is the one at low c/a (with the other minimum 0.3 mRy higher), while with GGA it is the one at high c/a (with the other minimum 0.7 mRy higher). The two energy minima are possible equilibrium states of hcp Cu; their positions are marked with arrows in the volume plot (lower panel in Fig. 1).

To find out whether these energy minima represent metastable or unstable phases we must check the stability conditions for hexagonal crystals,[5] which require calculations of the elastic constants. For hexagonal crystals the critical elastic constant for stability in our experience is the shear constant c_{44}, which we therefore calculate first. The procedure followed for this calculation was described in detail in Ref. 4, where we point out that the strains which must be applied

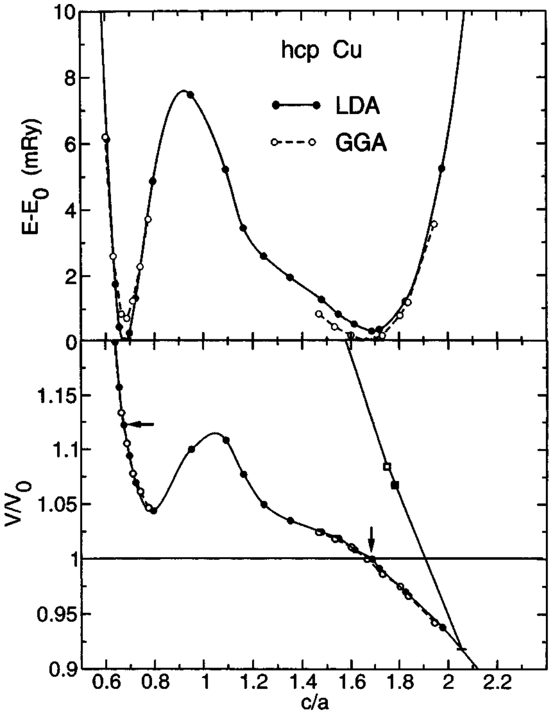

FIG. 1. Epitaxial Bain path of hexagonal Cu calculated with the LDA (solid) and the GGA (dashed) procedure. Top: energy/atom E relative to the energy/atom E_0 of lowest energy phase versus axial ratio c/a. Bottom: reduced volume V/V_0 versus c/a. The arrows show the positions of the energy minima. The open and full squares indicate the results of quantitative LEED analyses, and the straight line marks the error bars (see text).

for this purpose ($\epsilon_4 = \epsilon_5$) change the symmetry of the crystal from hexagonal to triclinic, and therefore allow distinction between unrelaxed and relaxed quantities. In the unrelaxed case the extra atom in each unit cell has the same strain as the other atom, i.e., the strain is homogeneous. In the relaxed case the extra atom may be expected to move away from the homogeneous position, but the choices of 60° angle and symmetric strains will keep the atom in the plane bisecting the 60° angle.

The calculations show that for both phases (low and high c/a) and for both LDA and GGA, both the unrelaxed and the relaxed c_{44} constants are negative (between -0.03 and -0.10 Mbar). These results indicate that both phases are unstable with respect to shears in the (a, c) and the (b, c) planes. It was therefore unnecessary to determine the remaining five elastic constants.

III. LEED EXPERIMENTS AND INTENSITY ANALYSIS

The calculated lattice constants of the high c/a phase are $a = 2.956$ Å and $c = 5.010$ Å from the LDA, and $a = 3.063$ Å and $c = 5.163$ Å from the GGA calculations. For brevity, we will consider only the LDA values (also because they have a somewhat smaller misfit to the unit mesh of W{001}, see below). The hexagonal phase with those lattice constants has a $(11\bar{2}0)$ rectangular unit mesh with sides $a' = 2a\cos 30° = 5.120$ Å along $[1\bar{1}00]$ and $b' = 5.010$ Å ($= c$) along [0001], with the extra atom at $a'/3$ and $b'/2$, as depicted in Fig. 2 (top).

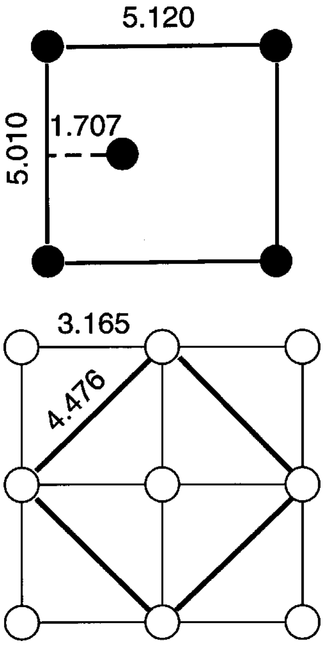

FIG. 2. Top: unit mesh of the $(11\bar{2}0)$ surface of the hexagonal phase of Cu with $c/a = 1.69$. Bottom: W{001} net, the 45° square (heavy lines) outlines the unit mesh assumed by the $(11\bar{2}0)$ net upon pseudomorphic epitaxy.

In order for this rectangular unit mesh to produce a $c(2\times 2)$ LEED pattern on W{001} it must be strained to fit onto the 45° square with sides equal to the diagonal of the substrate's square mesh. Figure 2 (bottom) illustrates the situation. The square unit mesh of W{001} has edges 3.165 Å long; hence the diagonal measures 4.476 Å (heavy lines in the figure). The strains created by fitting the $(11\bar{2}0)$ unit mesh discussed above on this 4.476 Å square are large: 12.6% along $[1\bar{1}00]$ and 10.7% along [0001], both compressive. With such large strains one would not expect pseudomorphic epitaxy to occur for more than one layer, if at all, but in view of the WHB report[1] we decided to test for pseudomorphism experimentally.

The experiment involved cleaning the suface of a W{001} platelet in ultrahigh vacuum, then depositing Cu incrementally with continous monitoring of the chemical state of the surface with Auger electron spectroscopy (AES) and of the crystalline state with LEED. The procedures are described in detail, e.g., in Ref. 6.

In the present case the LEED pattern from the clean substrate did not change its size while Cu was being deposited (in the sense that the unit mesh remained equal to that of the underlying substrate—an indication of pseudomorphic growth), but upon a coverage of about one monolayer a weak $c(2\times 2)$ pattern became visible. The integral-order beams were strong and sharp, the fractional-order beams weak and diffuse. With increasing thickness of the Cu film the background increased rapidly and the fractional-order beams were no longer visible, i.e., the pattern was 1×1, but beyond a thickness of about 20 Å a weak $c(2\times2)$ reappeared. At this stage the W signal in AES scans was no longer visible, the fractional-order beams were again weak and diffuse, but their $I(V)$ curves could be measured (only for the $\frac{1}{2}\,\frac{3}{2}$ and the $\frac{3}{2}\,\frac{3}{2}$ beams, not the $\frac{1}{2}\,\frac{1}{2}$, which, being near the specular 00 beam, was swamped in the high background). When the film thickness exceeded about 25 Å (estimated) the LEED pattern was completely obliterated.

We first attempted an intensity analysis of the 1×1 structure, taken as pseudomorphic to the W{001} substrate. The calculations of diffracted intensities were done with the CHANGE computer program written by Jepsen,[7] including 69 beams and 6 phase shifts up to 320 eV, with the Cu potential obtained from the collection of Moruzzi, Janak, and Williams[8] (real part of the inner potential initially set at 10 eV and adjustable during the analysis; imaginary part 4 eV; root-mean-square amplitude of thermal vibrations $(\langle u^2\rangle)^{1/2}=0.15$ Å). With the in-plane lattice constant of the Cu film set equal to that of W{001}, $a=3.165$ Å, we tested many values of the bulk interlayer spacing d_{bulk}: from 0.60 to 2.20 Å, in steps of 0.1 Å, in each case varying the *change* in the first interlayer spacing Δd_{12} from -0.5 to $+0.5$ Å in steps of 0.05 Å. We found no fit of the calculated to the observed $I(V)$ curves. The growth was certainly pseudomorphic, hence the in-plane parameter was known, but no interlayer spacing was found that would fit the experimental data. We can, of course, not exclude that some different, untested 1×1 structure may have contributed to the measured $I(V)$ curves, but the fact that the $I(V)$ curves of the 1×1 structure (when the fractional-order beams could not be seen over the high background) were very similar to those of the integral-order beams of the $c(2\times2)$ structure strongly suggested the possibility of an hexagonal $(11\bar{2}0)$ film.

For this case we took an in-plane parameter of 4.476 Å, kept the extra atom in the 1/3 1/2 position in this unit mesh, and used 161 beams in the calculations. Note that the comparison between theoretical and experimental $I(V)$ curves must take into account the difference between the experimental cubic indexing and the theoretical hexagonal indexing. The relation between the two can be easily found by looking at a sketch of the corresponding LEED patterns. Such a sketch can be found in Ref. 2; in the present case the relations are (using *c* and *h* to identify cubic and hexagonal indices, respectively): $10c=11h$; $11c=(02+20)h$; $20c=22h$; $21c=(13+31)h$; $(\frac{1}{2}\frac{3}{2})c=(21+12)h$; $(\frac{3}{2}\frac{3}{2})c=30h$.

A minimum in the Zanazzi-Jona r_{ZJ} factor[9] was found with parameters $d_{\mathrm{bulk}}=1.28$ Å $\Delta d_{12}=-0.15$ Å, $r_{\mathrm{ZJ}}=0.17$. If we consider *only* the two fractional-order beams (to avoid contributions of unknown 1×1 structures) we find $d_{\mathrm{bulk}}=1.26$ Å, $\Delta d_{12}=-0.15$ Å, $r_{\mathrm{ZJ}}=0.06$. Changes in the position of the extra atom (to which LEED is very insensitive at normal incidence) and consideration of changes in the second interlayer spacing 23 did not alter these results. The error bars are large, estimated to be between ±0.1 and ±0.2 Å, owing to the very high background in the LEED pattern. Comparison between theoretical and experimental $I(V)$ curves can be made visually in Fig. 3. We note that the agreement is only mediocre, as already indicated by the *R* factor; that this is due to the high background is confirmed by the fact that the positions of the major peaks are well-matched, but the intensities, which depend strongly on the background subtraction, are not.

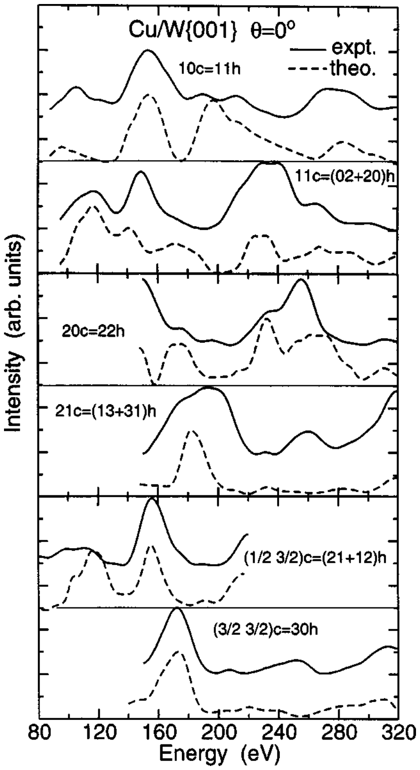

FIG. 3. Experimental and theoretical $I(V)$ curves for the Cu film grown on W{001}. In the beam indices, *c* refers to cubic (experimental), *h* to hexagonal (theoretical) indexing.

IV. DISCUSSION

To determine which of the hexagonal Cu phases was stabilized by constrained epitaxy in the present experiments we enter the experimental results in the calculated V/V_0-versus-c/a plot of Fig. 1 (bottom). The volume/atom in the grown film is $V=(4.476)^2\times1.28/2=12.82$ Å^3. The experimental value of V_0 for the high-c/a phase is unknown, hence we take in its place the experimental value of the fcc Cu ground state, $V_0=11.81$ Å^3, thereby finding $V/V_0=1.085$. To find the value of c/a we note that in this case $c=4.476$ Å, while $a=2\times d_{\mathrm{bulk}}=2.56$ Å; hence $c/a=1.75$. This point is entered as the open square in Fig. 1 (bottom). The point corresponding to the value of $d_{\mathrm{bulk}}=1.26$ Å found with the fractional beams only is plotted as the full square. The error bars are drawn for the case $\Delta d_{\mathrm{bulk}}=\pm0.2$ Å. The important result is that the experimental points are on the same side of the volume curve as the high-c/a phase, proving that the present experiments have stabilized that phase by constrained epitaxy, even if only in few small regions. The very surprising aspect of this conclusion is that in spite of the instability of the phase and the large misfits to the substrate net, the strained phase grew pseudomorphically and could still be detected in rather thick films, whereas conventional wisdom would predict that at best one or two layers, if any, could possibly be stabilized in these experiments. We confirm the result of WHB that an hcp Cu phase grows on W{001}, but in our case pseudomorphically.

ACKNOWLEDGMENT

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