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Metastable body-centered-tetragonal phase of vanadium on Cu{001}

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Pseudomorphic ultrathin films of vanadium on Cu{001} up to about 14 Å thick have a body-centered-tetragonal structure with $a=2.556$ Å and $c=4.40\pm0.10$ Å, as determined by quantitative low-energy electron-diffraction analysis. Despite the low accuracy of the quantitative results, which is due to the high densities of defects and disorder in the grown films, use of the epitaxial Bain path leads to unambiguous identification of the films' structure as a strained state of the metastable equilibrium bct phase of vanadium at $c/a=1.78$, rather than a strained state of the bcc ground state at $c/a=1$. [S0163-1829(99)03620-6]

INTRODUCTION

In a recent publication[1] we reported the stabilization of a metastable phase of bulk vanadium with body-centered-tetragonal (bct) structure by means of epitaxy on Ni{001}. The existence of this phase had been predicted theoretically by total-energy calculations of tetragonal states and the resulting so-called epitaxial Bain path (EBP) for vanadium.[2,3] In view of the remarkable result of this recent work, which indicated the existence of an equilibrium phase of V very different from the bcc ground state, it seemed worthwhile to confirm this result on another substrate. Possibly, use of a substrate on which the epitaxial film of V would be in tension rather than in compression (as on Ni{001}) would produce a more ordered film. Hence Cu{001} with an in-plane lattice parameter 2.8% larger than Ni{001} seemed appropriate.

Epitaxial Bain paths can be generalized for different surfaces of different crystal structures, but have so far been limited to {001} surfaces of tetragonal structures, such as the case of pseudomorphic epitaxy of a cubic material on a substrate surface with a square unit mesh. In this case the EBP is the curve on the tetragonal plane (the plane with the tetragonal lattice constants a and c as coordinates) that passes through all the tetragonal states produced by epitaxial strain on the unstrained (the so-called equilibrium) phases of the material.

One way to present the EBP is to plot a curve on the tetragonal plane $c=c(a)$: For any value a of the square mesh that may be imposed by the pseudomorphism on the film material, the curve gives the value of the c parameter that minimizes the total energy of the system. The minimum then corresponds to the epitaxial condition of zero stress normal to the epitaxial film. Another way to present the EBP is to plot the normalized volume per atom V/V_0 (V is the volume per atom in the strained state and V_0 is the volume per atom in the stable equilibrium state) versus the axial ratio c/a. In either case the curve passes through two points that correspond to two total-energy minima: The lower minimum defines the stable tetragonal equilibrium state, the other, a metastable equilibrium state; both are states of bulk crystalline V. Between the two minima there is a saddle point, which corresponds to an unstable state and is surrounded by a region of inherently unstable states that cannot be stabilized by applied stress. The advantage of using reduced units for the coordinates is that theory can be compared more accurately with experiment, since first-principles theory systematically underestimates lattice constants.

Thus the tetragonal plane is divided into three regions: two regions of strained phases, maintained by epitaxial stress, separated by a region of inherently unstable states. This division has important practical consequences: If a pseudomorphic film is grown on a square net with parameter a and the c parameter is known [e.g., from a quantitative low-energy electron diffraction (QLEED) analysis], then the pair a,c represents a point on the tetragonal plane that is not in the unstable region. The observed structure has an unambiguous identification as either a strained state of the stable equilibrium phase or a strained state of the metastable equilibrium phase. Since the lattice parameters of both phases are known (from the total-energy calculation of the EBP), it is easy to calculate the strain in the grown film.

For vanadium[3] the energy along the EBP displays the lower minimum at $c/a=1.0$, $c=a=2.92$ Å (see Fig. 1), which is the stable body-centered-cubic (bcc) phase of that metal, and the shallower minimum (by 10 mRy/atom) at

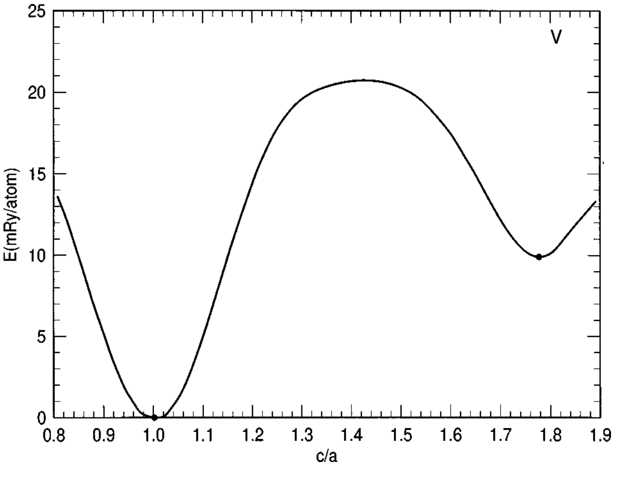

FIG. 1. Total energy E of tetragonal V along the epitaxial Bain path as a function of c/a, showing that the metastable equilibrium state at $c/a=1.78$ has energy 10 mRy/atom above the stable equilibrium state at $c/a=1$. The full circles mark the phase points at the minima of E, which appear again in Fig. 3.

$c/a=1.78$ and $V/V_0=1.02$, whence we calculate (with $V_0=12.50\,\text{Å}^3$, the theoretical value of the bcc volume per atom given in Ref. 3) that $a=2.43\,\text{Å}$ and $c=4.33\,\text{Å}$ for the metastable body-centered-tetragonal (bct) phase of vanadium. Since, as pointed out in Ref. 1, the lattice constant calculated with the local-density approximation is found for bcc V to be 3.3% too low with respect to experiment, the values of the experimental lattice parameters for the bct phase are predicted to be $a=2.51\,\text{Å}$ and $c=4.47\,\text{Å}$.

In our first attempt at stabilizing this bct phase[1] we chose a Ni{001} surface as a substrate on which to grow a vanadium film, because the primitive square mesh on Ni{001} has sides $a=2.49\,\text{Å}$, hence only 0.8% smaller than the sides of the square mesh of the V bct phase. Despite this small misfit, vanadium films could be grown only to thicknesses of about 20 Å before defects destroyed the long-range order and the low-energy electron diffraction (LEED) pattern was obliterated. As a consequence, the results of the QLEED analysis were tagged with large error bars. However, the attempt to grow the metastable bct phase was nevertheless successful, because the experimental data were found to fall in the region around the metastable equilibrium state and on the compressive side of the equilibrium point, thus proving that the structure of the vanadium film was a strained state of the metastable phase.

Another possible choice of substrate for the stabilization of bct V is Cu{001}, which has a primitive square mesh with sides $a=2.56\,\text{Å}$. Thus, while on Ni{001} the epitaxial strain of the V film is a 0.8% compression, on Cu{001} the epitaxial strain is about a 2% expansion. Compared to Ni{001} as substrate, the sign of the misfit is more favorable for the growth of better-ordered films. The magnitude is not as favorable, but still well within the range of epitaxial film growth, hence we decided to try a Cu{001} substrate.

Previous work on the V/Cu{001} system was not encouraging. Pervan, Valla, and Milun[4] reported observing 1×1 LEED patterns for one-layer-thick V films and complex LEED patterns corresponding to four domains of bcc{110} V for films two to three atomic layers thick. However, the V coverage was determined from the decrease of a Cu Auger line with an assumed electron mean free path (a procedure that we have often found to have low accuracy) and the LEED work was only qualitative, i.e., LEED intensities were not measured. Our work described below shows that before collapsing into bcc{110} (with four rotationally related domains), ultrathin V films on Cu{001} have a structure derived from strained metastable bct V, as predicted by the EBP, although the films have many defects and poor crystallinity.

EXPERIMENT

A Cu{001} platelet ($10\times5\times1\,\text{mm}^3$), mounted in a vacuum system capable of reaching a base pressure of 1×10^{-10} Torr, was cleaned *in situ* with sequences of argon-ion bombardments (8×10^{-5} Torr, 375 eV, 1 μA/cm^2) and annealings (10 min at about 650 °C) until Auger electron spectroscopy (AES) revealed no impurities above the noise and a sharp low-background LEED pattern was observed. The vanadium source was a V wire (0.25 mm diameter) heated by electric current to about 1250 °C. Exposure times varied between 10 and 30 min, producing deposition rates between 0.3 and 1.3 Å/min. The substrate was kept at room temperature during deposition.

Estimates of film thickness were based on the ratios of AES intensities as explained elsewhere.[5] In the present case two pairs of AES intensities were considered, V(31 eV)/Cu(60 eV) and V(473 eV)/Cu(920 eV), the former being judged more reliable than the latter, owing to the closeness of the AES energies to one another. Film thicknesses varied between 3 and 18 Å in the course of the experiments.

The LEED pattern remained 1×1 with increasing V deposition, but with rapidly increasing background. When the film thickness increased beyond about 16 Å extra spots appeared on the LEED pattern, which indicated the presence of four domains of bcc{110} vanadium, as reported by Pervan, Valla, and Milun.[4] During collection of intensity data from the 1×1 pattern the same difficulty was encountered as in the study of V on Ni{001},[1] namely, the LEED background increased so rapidly with surface coverage (indicative of rapid formation of defects and disorder in the film) that there was only a very narrow range of coverages at which the film was thick enough for the $I(V)$ curves to be stable (i.e., to correspond to semi-infinite thickness) and yet the LEED pattern was still good enough for $I(V)$ measurements to be carried out. The intensity data used in the analysis described below were collected from a film about 14 Å thick. The high background introduced a rather large uncertainty in the widths and positions of peaks in the $I(V)$ curves, so that the overall accuracy of interlayer spacings is expected to be lower than the norm in surface and overlayer studies, as was the case for V on Ni{001}.

We measured the intensities of the 10, 11, and 20 beams at normal incidence and of the 00 beam at non-normal incidence as functions of incident-electron energy [the so-called $I(V)$ curves or spectra] at all stages of deposition to monitor their changes. The experimental procedure consisted in making a first deposition, determining the film thickness with AES, checking the LEED pattern, and collecting $I(V)$ spectra. A second deposition was then made and all steps repeated, etc. Eventually, the LEED pattern deteriorated to the point of being unusable, at which point the sample was recleaned to the bare substrate surface and the whole process repeated.

QLEED ANALYSIS

The calculations of diffracted intensities were made with the full-dynamical program CHANGE (Ref. 6) including 69 beams and 6 phase shifts up to 500 eV (tests with 8 phase shifts did not reveal significant differences). The Cu and V potentials needed for the corresponding phase shifts were obtained from the collection of Moruzzi, Janak, and Williams.[7] The real part of the inner potential was initially chosen at 10 eV (adjustable during the analysis; the final value was 15±4 eV), the imaginary part was 3 eV, and the root-mean-square amplitude of thermal vibrations $\langle u^2\rangle^{1/2}=0.11\,\text{Å}$.

The calculations assumed that the V film was semi-infinite with an in-plane lattice constant of 2.556 Å imposed by the pseudomorphism with the Cu{001} substrate. The interlayer spacing d_{bulk} was varied from 2.02 to 2.24 Å in steps of 0.02 Å, in each case varying the change Δd_{12} of the first

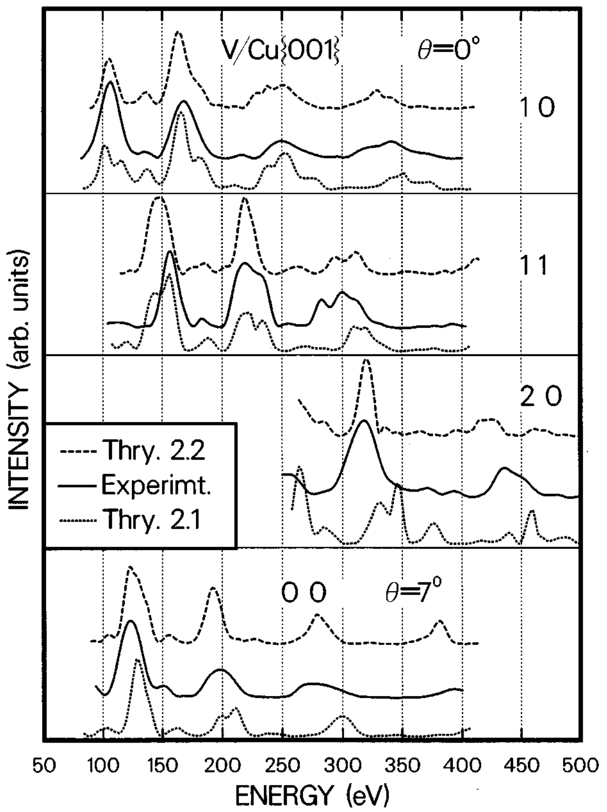

FIG. 2. Experimental (solid) and theoretical (dashed and dotted) $I(V)$ spectra: 10, 11, and 20 at normal incidence ($\theta = 0°$), and 00 at off-normal incidence ($\theta = 7°$, $\phi = -17.5°$). Dotted curves were calculated with $d_{\mathrm{bulk}} = 2.10$ Å, dashed curves with $d_{\mathrm{bulk}} = 2.20$ Å.

interlayer spacing d_{12} from -0.18 to 0.06 Å in steps of 0.03 Å. The structure refinement was done with the 10 and 11 beams only since the 20 beam was judged less reliable owing to a very low signal-to-noise ratio.

The agreement between calculated and observed $I(V)$ spectra was gauged both visually and by R-factor analysis with three R factors: R_{VHT},[8] r_{ZJ},[9] and R_P.[10] The R-factor minima vary considerably: $R_{VHT} = 0.37$ for $d_{\mathrm{bulk}} = 2.20$ Å and $\Delta d_{12} = -0.09$ Å; $r_{ZJ} = 0.19$ for $d_{\mathrm{bulk}} = 2.12$ Å and $\Delta d_{12} = -0.09$ Å, and $R_P = 0.53$ for $d_{\mathrm{bulk}} = 2.10$ Å and $\Delta d_{12} = +0.06$ Å. In all cases, the error bars are put at ±0.05 Å. Changes of the d_{23} spacing did not improve the fit.

Figure 2 depicts calculated and observed $I(V)$ curves: 10, 11, and 20 at normal incidence ($\theta = 0°$) and 00 at $\theta = 7°$ and $\phi = -17.5°$. Dashed curves are theoretical for $d_{\mathrm{bulk}} = 2.20$ Å and dotted curves are theoretical for $d_{\mathrm{bulk}} = 2.10$ Å. The visual evaluation finds the overall fit (i.e., including the 20 beam at normal and the 00 beam at off-normal incidence) for $d_{\mathrm{bulk}} = 2.20$ Å better than that for $d_{\mathrm{bulk}} = 2.10$ Å (or 2.12 Å, not shown here).

CONCLUSIONS

The conclusions are similar to those drawn from the study of V on Ni{001}. Vanadium grows pseudomorphically on Cu{001} to thicknesses of about 14 Å, but also with high densities of defects and disorder, probably as a consequence of the small energy barrier between the strained metastable state and the bcc ground state. The structure of the V films is bct, with $a = 2.556$ Å (dictated by the Cu substrate) and c between 4.20 and 4.40 Å. As in the case of V/Ni{001}, the large uncertainty in the value of the c parameter is due to the poor quality of the LEED pattern produced by the V film and by the fact that only two $I(V)$ spectra could be used in the analysis, which is an inferior data base for quantitative surface-structure work.

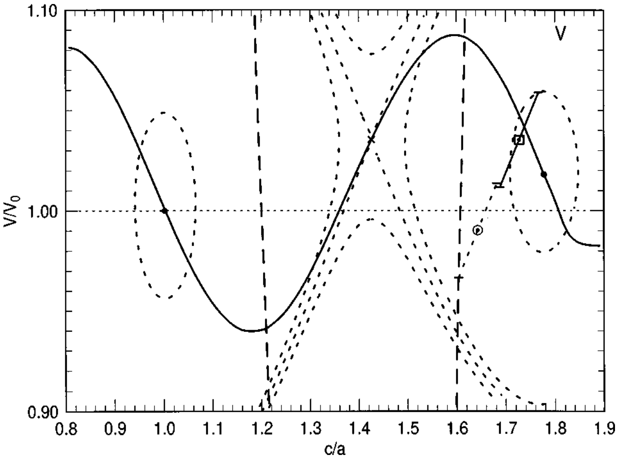

FIG. 3. Epitaxial Bain path for vanadium (Ref. 3) (solid curve) with stable bcc state at $c/a = 1.0$, metastable bct state at $c/a = 1.78$ (full circles), and unstable fcc state at $c/a = 1.414$ (saddle point, marked ×). Energy contours are drawn with short dashes at $\delta E = 1$ mRy above the stable and the metastable points, through the saddle point, and at $\pm\delta E$ from the saddle point. The region between the lines of long dashes, which includes the saddle point, contains inherently unstable states. The open square is the experimental result found in this work corresponding to $c = 4.40$ Å and the open circle corresponds to $c = 4.20$ Å. The error lines correspond to $\delta c = \pm 0.1$ Å.

The experimental results are plotted on the c/a-V/V_0 plane in Fig. 3 along with the EBP for V, the upper empty square corresponds to the $d_{\mathrm{bulk}} = 2.20$ Å value and the lower empty circle to the $d_{\mathrm{bulk}} = 2.10$ Å value, in both cases with error bars of ±0.05 Å. Despite the large uncertainty about the precise values of c/a and V/V_0, it is clear that the experimental points fall on the right-hand side of the unstable region, i.e., in the vicinity of the metastable bct state predicted by theory to occur at $c/a = 1.78$, and on the side of the equilibrium point corresponding to *tensile* stress, as expected on Cu{001}. Thus the growth of ultrathin films of vanadium on Cu{001} has produced a strained form of the metastable bct state of vanadium metal.

This result provides (along with the case of V/Ni{001}) another demonstration of the power of first-principles theory and of the usefulness of epitaxial Bain paths in predicting the existence of metastable phases and in interpreting the bulk structure of pseudomorphic films. Conversely, this result confirms the reliability of first-principles theory and provides a deeper understanding of the nature of a phase and its equilibrium and strained states.

ACKNOWLEDGMENT

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