Metastable phase of vanadium

Y. Tian, F. Jona, and P. M. Marcus

Department of Materials Science and Engineering, State University of New York, Stony Brook, New York 11794-2275

(Received 22 May 1998)

The epitaxial Bain path for vanadium, calculated by first-principles theory, reveals the existence of a metastable body-centered-tetragonal (bct) phase with $c/a = 1.78$. Experiments aimed at stabilizing this phase by pseudomorphic epitaxy on a Ni{001} substrate were successful insofar as the ultrathin films grown have a bct structure with c/a between 1.73 and 1.77. The bulk structure of the V films was determined by quantitative low-energy electron diffraction, but the accuracy of the results is worse than usual owing to high densities of defects in the grown films. [S0163-1829(98)03044-6]

I. INTRODUCTION

A crystal film that grows epitaxially and pseudomorphically on a surface of another crystal (the so-called substrate) is almost always strained because the surface mesh of the substrate seldom matches perfectly the surface mesh of the film material in its unstrained state (the film's equilibrium state). The strain arises from this mismatch of the surface meshes when the film material is forced to adopt the dimensions of the substrate mesh, as required by pseudomorphism.

But the film material may have more than one phase, hence more than one equilibrium state.[1] For example, metal crystals with body-centered-tetragonal (bct) structure have two bct phases, one with a stable equilibrium state and one with a metastable equilibrium state,[2–6] which correspond to two total-energy minima in the so-called tetragonal plane (defined by the tetragonal lattice constants a and c). Thus, when such a material grows pseudomorphically on a given substrate a question that arises is: Which phase does its equilibrium state belong to? The answer is one of two pieces of information that are required in order to determine the strain in the grown film. The other piece is knowledge of the interatomic distances in the bulk of the film, i.e., the film's atomic structure.

Since pseudomorphic films of metastable phases are likely to be ultrathin, i.e., to involve only up to 10 or 20 atomic layers, the determination of their atomic structure must be done with surface-sensitive probes, of which the most developed and the most successful is quantitative low-energy electron diffraction (QLEED).[7] In the case of films with the bct structure grown on square nets, which are the films considered in the present work, the only quantities to be determined are the interlayer spacings. In particular, to compare with bulk phases we want the bulk interlayer spacing or the c parameter, which is twice the interlayer spacing. QLEED can usually measure the interlayer spacing with an accuracy of about ± 0.03 Å.

Procedures for carrying out the strain analysis once the crystallography is known are described, e.g., in Ref. 8. Such procedures require knowledge of the elastic constants of the film's equilibrium state, and assume that linear elasticity theory holds (i.e., that the elastic constants do not change as the strain increases). Thus, it was found that ultrathin films of Fe and Co on Rh{001} have bct structures derived from bcc Fe and fcc Co, respectively, that Co films on Fe{001} and on TiAl(010) are derived from a metastable bct phase, and that Ti films on Al{001} are strained fcc Ti (see references cited in Ref. 8).

However, a better procedure, which does not require knowledge of elastic constants and does not assume linear elasticity theory, consists of comparing the measured structure of the film with the bct states on the so-called epitaxial Bain paths (EBP's).

Perhaps the best way to explain the EBP's is to describe how they are obtained. We do so here for the special case of tetragonal states. Consider, for simplicity, a material with cubic structure and lattice constant a_0. Suppose that we grow a pseudomorphic film of that material on a substrate surface with a square unit mesh with sides equal to $a_1 \neq a_0$. Since the film material is strained in the plane parallel to the substrate surface, the elastic response will change the spacing in the perpendicular direction, so that the film will assume a body-centered tetragonal structure, i.e., a unit cell with a square base $a_1 \times a_1$ and height given by $c_1 \neq a_1$. The question is, what is the value of c_1?

Nature will of course produce the value of c_1 that minimizes the total energy of the system, and we can do a total-energy calculation to find out what that value is. We then have one pair of values, a_1 and c_1, which we can plot as a point on the tetragonal plane with coordinates a and c. Next consider a substrate with a square unit mesh with sides a_2, find, with a total-energy calculation, the value of c_2 that minimizes the total energy of this system and plot the point (a_2, c_2) on the tetragonal plane. Repeat the procedure for a_3, etc.

The curve passing through the plotted points is the EBP for the material selected. Each point on the EBP is associated with the value of the total energy of the particular tetragonal state represented by that point. Usually, and specifically in the case of V, two points on the EBP correspond to two total-energy minima: the lower one defines the stable tetragonal equilibrium state and the other, a metastable equilibrium state. Thus we can define the EBP as the curve on the tetragonal plane that passes through all the tetragonal states produced by epitaxial strain on the equilibrium states of the material.

The EBP is particularly useful in studies of epitaxial growth, indeed because for any value a of the square-mesh size that may be imposed on the film material (constrained by the substrate net) the curve gives the values of the c parameter that minimizes the total energy E of the system,
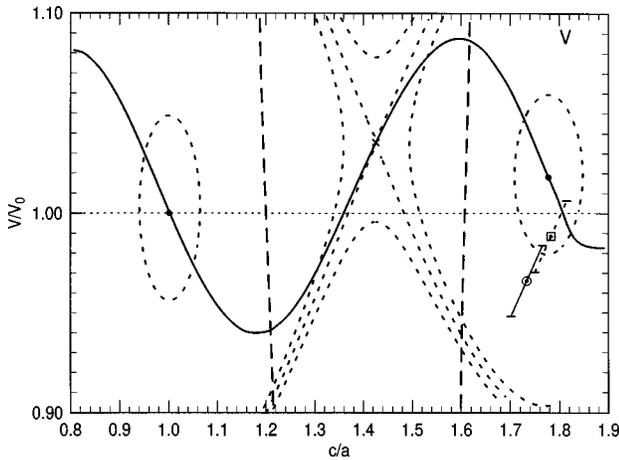
FIG. 1. Epitaxial Bain path for vanadium (Ref. 6) (solid curve) with stable bcc state at $c/a = 1.0$, metastable bct state at $c/a = 1.78$ (full circles), and unstable fcc state at $c/a = 1.414$ (saddle point, marked ×). Energy contours are drawn with short dashes at $\delta E = 1$ mRy above the stable and the metastable points, through the saddle point and at $\pm \delta E$ from the saddle point. The metastable equilibrium state has energy 10 mRy/atom above that of the stable state. The region between the lines of long dashes, which includes the saddle point, contains inherently unstable states. The open circle and the square are experimental points found in this work and discussed in the text.

hence corresponds to the observed structure of the constrained system. Reference 5 introduces EBP's calculated from first principles and applies them to the measured structures of epitaxial films. Reference 6 gives a detailed analysis of the EBP and its properties. Reference 9 discusses how the EBP can be used to identify a new phase of Ti, and shows how the total energy and other properties of tetragonal Ti vary along the EBP.

One way to present EBP's is in fact to plot the c value for which E has a minimum as a function of a (see, e.g., Ref. 8). Another way is to plot the normalized volume per atom V/V_0 versus a (Ref. 5) or versus the ratio c/a (V_0 is the volume per atom of the equilibrium state of the stable phase of the film material under study), as done in Ref. 6. An advantage of using reduced variables in the plot is that it compensates for the systematic underestimate of lattice constants by first-principles theory based on the local-density approximation (LDA). An example pertinent to the present work is given in Fig. 1, as calculated by Marcus and Alippi[6] for the metal vanadium. The EBP (solid curve) passes through the two equilibrium states at the energy minima (full circles) and through the saddle point (cross) between the two minima. The segment of the EBP that has a positive slope (the volume increases with increasing c/a) and includes the saddle point consists of inherently unstable phases. This unstable region separates two regions of strained phases, one around the stable equilibrium state (in the case of vanadium, in Fig. 1, the unstrained bcc state with $c/a = 1$), the other around a metastable equilibrium state (in Fig. 1 at $c/a = 1.78$).

The usefulness of the EBP's can be seen as follows. An ultrathin film grown on a square substrate with parameter a and for which the c parameter is known, as measured, e.g., by QLEED, is represented by a point on the c/a-V/V_0 plane (where V_0 is the *experimental* bcc volume per atom). If this

point lies in the region around the stable equilibrium state, then the film's strained structure is obviously derived from the stable phase, while if it lies in the region around the metastable equilibrium state then the film's equilibrium state belongs to the metastable phase. Since the two regions are disjoint, the structure point must lie in just one region. The strain in the film is then easily calculated: if a_{eq} and c_{eq} are the lattice parameters of the equilibrium phase, then the strains are, in the plane of the surface, $\epsilon_\parallel = (a - a_{eq})/a_{eq}$, and perpendicular to the surface, $\epsilon_\perp = (c - c_{eq})/c_{eq}$.

Thus, the EBP's are directly useful in determining the bulk equilibrium structure of pseudomorphic films. But their main value lies in predicting metastable bct phases that might be otherwise unknown, and in guiding the experimentalist in designing experiments aimed at stabilizing such metastable phases. The present work is in fact a demonstration of the latter use of EBP's.

Figure 1 reveals that vanadium has a metastable bct phase with $c/a = 1.78$ and $V/V_0 = 1.02$, from which we calculate (with $V_0 = 12.58$ Å^3, the *theoretical* value of the bcc volume per atom) that $a = 2.43$ Å and $c = 4.33$ Å. In searching for a suitable substrate on which to attempt the stabilization of this metastable phase one must keep in mind that theoretical estimates of lattice constants based on the LDA are usually too low with respect to experiment by about a few percent. In the case of the (stable) bcc phase of vanadium, the theory is 3.3% too low compared with experiment (2.93 versus 3.03 Å).[4–6] (Not all band-structure programs using the LDA give this large an underestimate of the lattice constant.[10]) Assuming that the same percentage applies to the bct phase, we find that the probable experimental values of the parameters are $a = 2.51$ and $c = 4.47$ Å. A suitable substrate appears therefore to be Ni{001}, which is fcc with $a_0 = 3.52$ Å, hence with a primitive square mesh with edge $a = 2.49$ Å, and we can expect the film to be in slight epitaxial compression.

Figure 2 of Ref. 5 and Table II of Ref. 6 give the energies of the bct equilibrium state and the barrier height between the equilibrium states relative to the bcc equilibrium state. The bct state is 10 mRy/atom and the barrier top is 20.8 mRy/atom above the bcc state. This substantial barrier suggests that a bct vanadium film should remain stabilized once formed.

The work described below is a study of the growth of vanadium ultrathin films on Ni{001}. The experiment and its difficulties are described in Sec. II, the QLEED analysis in Sec. III, and the conclusions in Sec. IV.

II. EXPERIMENT

A Ni{001} platelet ($12 \times 5 \times 1$ 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 anneals (10 min at approximately 700 °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 wire (initially, diameter 0.13 mm, later, 0.25 mm) heated by electric current to about 1250 °C. Exposure times varied between 15 and 30 min, producing deposition rates between 0.6 and 1.3 Å/min. The sample was kept at room temperature during deposition of V.

Estimates of film thickness, based on ratios of AES intensities,[11] were inaccurate, because the available equipment allowed only measurement of the ratio between the AES line of V at 473 eV and the AES line of Ni at 848 eV, a ratio that varied between 3 and 13 in different experiments. The large difference in energy between the two AES lines led in this case to overestimates of the film thickness. Film thicknesses so determined varied between 13 and 28 Å in the course of the experiments, but were considered *nominal* and used merely as relative reference numbers.

The LEED pattern remained 1×1 with increasing V deposition, but with rapidly increasing background. The intensities of diffracted beams (with indices 10, 11, and 20, whenever possible) were measured at normal incidence as functions of incident-electron energy [so-called $I(V)$ curves or spectra] at all stages of deposition to monitor their changes. In general, if the growth is pseudomorphic, it is expected that the $I(V)$ curves would change, with increasing surface coverage, with respect to those from the clean surface, and would keep changing until the film becomes thick enough to be considered semi-infinite, i.e., when the incoming electrons no longer "see" the film-substrate interface [usually, this happens when the film is thicker than 6–8 atomic layers, and the resulting $I(V)$ curves are then "stable"].

Thus, the experimental procedure consisted in making a first deposition, determining the *nominal* 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 re-cleaned to the bare substrate surface and the whole process repeated.

The main difficulty encountered in this work was due to the fact that 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 for which the film was thick enough and yet the LEED pattern still good enough for $I(V)$ measurements to be carried out. Unfortunately, our control of the deposition source (the subliming V wire) was too coarse to allow precise and reproducible coverages in the range desired.

For example, when the *nominal* thickness was 13 Å, the background in the LEED pattern was not too high and the $I(V)$ spectra were different from those of the clean Ni{001} surface, but further deposition obliterated the LEED pattern (coverage too high). With a *nominal* thickness of 19 Å, the $I(V)$ curves were different from those of the clean substrate and different from those measured with the 13-Å film, but the next deposition turned out to be again too large. In total, we repeated the growth experiments seven times, and we found that when the *nominal* film thickness was between 23 and 28 Å, the measurable $I(V)$ spectra were reasonably "stable." But the background was very high, only the 10 and the 11 beams were measurable (the higher-index beams were only barely visible to the eye above the background). It is estimated that the effective thickness of the V film was about eight atomic layers at that point.

The high background introduced additional uncertainty in the widths and positions of peaks in the $I(V)$ curves, so that
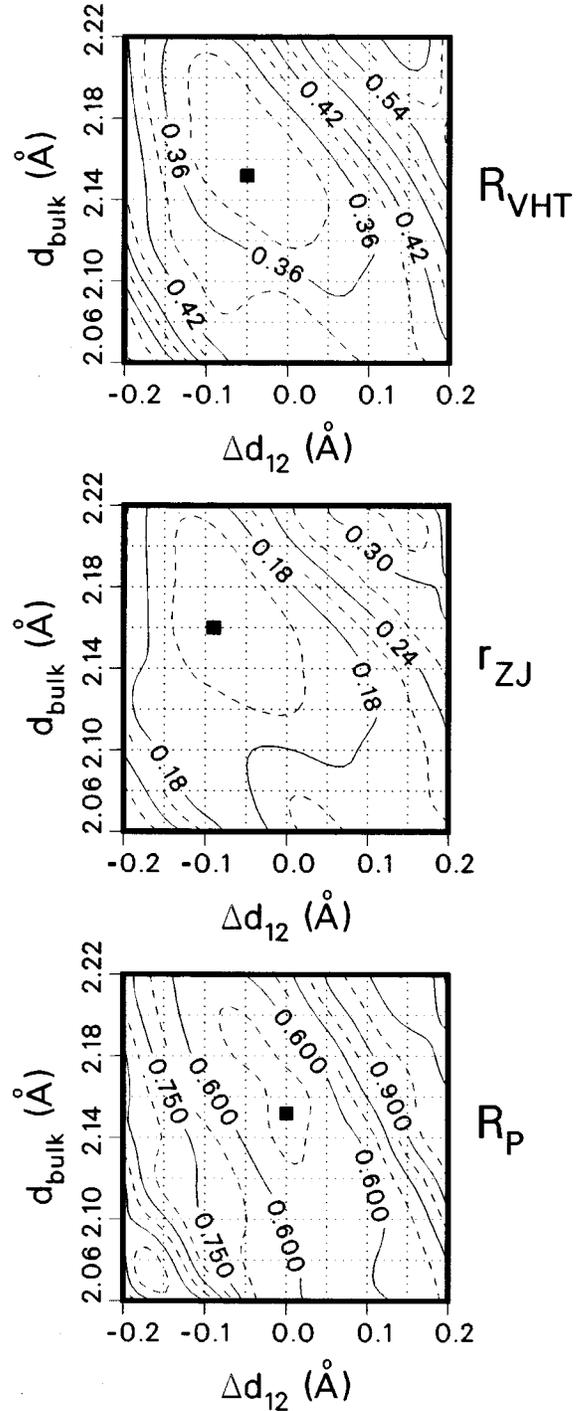

FIG. 2. Contour plots of the three R factors used in this work, as indicated on the right of each plot (see text). The abscissa is the change Δd_{12} of the first interlayer spacing d_{12} from its bulk value, the ordinate is the bulk interlayer spacing d_{bulk}.

the overall accuracy of interlayer spacings is expected to be lower than the norm in surface and overlayer studies.

III. QLEED ANALYSIS

The calculations of diffracted intensities were made with the full-dynamical program CHANGE (Ref. 12) including 57

beams and 6 phase shifts up to 400 eV (tests with eight phase shifts up to 400 eV did not reveal significant differences). The Ni and V potentials needed for the corresponding phase shifts were obtained from the collection of Moruzzi, Janak, and Williams.[13] The real part of the inner potential was initially chosen at 10 eV (adjustable during the analysis—the final value was 7 ± 3 eV), the imaginary part was 3 eV, and the root-mean-square amplitude of thermal vibrations $(\langle u^2 \rangle)^{1/2} = 0.11$ Å.

The calculations assumed that the V film was semiinfinite with an in-plane lattice constant of 2.49 Å imposed by the pseudomorphism with the Ni{001} substrate. The interlayer spacing d_{bulk} was varied initially from 1.76 to 2.56 Å in steps of 0.05 Å, and later from 2.06 to 2.22 Å in steps of 0.02 Å, in each case varying the change Δd_{12} of the first interlayer spacing d_{12} from -0.2 to $+0.2$ Å in steps of 0.05 Å.

The agreement between calculated and observed $I(V)$ spectra was gauged both visually and by R-factor analysis with three R factors: R_{VHT},[14] r_{ZJ},[15] and R_P.[16] Contour plots for these three R factors in the d_{bulk}-Δd_{12} plane are depicted in Fig. 2, where two observations can be made: (1) the minima occur at $d_{bulk} = 2.15$–2.16 Å and $\Delta d_{12} = 0$ to -0.1 Å, but (2) the minima are rather flat, perhaps as a consequence of the poor accuracy in the experimental data. In fact, the R-factor values do not change significantly in the range of d_{bulk} between 2.16 and 2.21 Å, and Δd_{12} between -0.05 and -0.10 Å. The numbers are for $d_{bulk} = 2.16$ Å and $\Delta d_{12} = -0.05$ Å, $R_{VHT} = 0.31$, $r_{ZJ} = 0.13$, and $R_P = 0.55$; whereas for $d_{bulk} = 2.21$ Å and $\Delta d_{12} = -0.10$ Å, they are $R_{VHT} = 0.33$, $r_{ZJ} = 0.14$, and $R_P = 0.55$. In all cases, the error bars are set at ± 0.04 Å. Changes of the d_{23} spacing did not reduce the R factor significantly.

Figure 3 depicts the 10 and 11 $I(V)$ curves from the clean Ni{001} surface, and the calculated and observed 10 and 11 $I(V)$ curves for the V{001} film. The Ni curves are shown to demonstrate the difference between them and those of the V film. The calculated (dotted) curves are (a) for $d_{bulk} = 2.16$ Å and $\Delta d_{12} = -0.05$ Å; (b) for $d_{bulk} = 2.21$ Å and $\Delta d_{12} = -0.10$ Å. Although somewhat different from each other, they are both reasonable fits to their experimental counterparts.

IV. CONCLUSIONS

Vanadium does grow pseudomorphically on Ni{001} to thicknesses estimated to be about eight atomic layers, albeit with high densities of defects and disorder. The structure of the V films is bct, with $a = 2.49$ Å (dictated by the Ni substrate) and c between 4.32 and 4.42 Å. 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
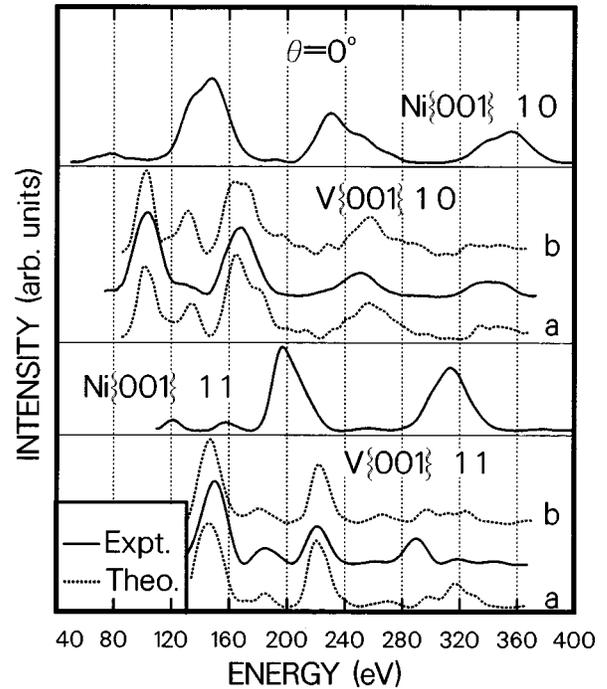

FIG. 3. Experimental (solid) and theoretical (dashed) $I(V)$ spectra. The Ni{001} $I(V)$ spectra are presented to show their difference from the corresponding $I(V)$ spectra of the V{001} film. Curves labeled a were calculated with $d_{bulk} = 2.16$ Å, while curves labeled b were calculated with $d_{bulk} = 2.21$ Å.

only two $I(V)$ spectra could be used in the analysis—which is an inferior data base for quantitative surface-structure work.

The experimental results are plotted on the c/a-V/V_0 plane in Fig. 1, the circle for the $d_{bulk} = 2.16$ Å value and the square for the $d_{bulk} = 2.21$ Å value, in both cases with error bars of ± 0.04 Å. Despite the large uncertainty about the precise values of c/a and V/V_0, it is clear that the experimental points fall in the vicinity of the metastable bct state predicted by theory to occur at $c/a = 1.78$. In addition the error line, due entirely to uncertainty in c, points toward a slightly compressed state on the EBP. This state is in fact overlapped when the slightly less favored c value is used. Thus the growth of ultrathin films of vanadium on Ni{001} has produced a strained form of a new metastable state of vanadium metal.

This result provides a good 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 determined, for example, by quantitative low-energy electron diffraction. It would be highly desirable to have available epitaxial Bain paths for all metals in the $3d$, $4d$, and $5d$ series.

[1] To discuss the structure of epitaxial films we use the following terminology. A crystalline material has a discrete set of phases. Each phase has one equilibrium state which is unstrained, hence is maintained without applied forces. Each phase also has a continuous region of strained states in which the structure is deformed from the equilibrium state and is maintained by applied forces.

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