Identification of metastable phases: face-centred cubic Ti

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Abstract. First-principles total-energy electronic structure calculations are used to find the epitaxial line of tetragonal Ti, i.e., the line of body-centred tetragonal (bct) structures produced by isotropic epitaxial strain on the (001) plane of tetragonal phases of Ti. An fcc phase and a higher-energy noncubic bct phase are found at minima of the total energy with respect to tetragonal deformations, but the bcc structure is found to be a saddle point of energy. The calculation yields the strained structures, the corresponding stresses, and the elastic stiffness coefficients on the epitaxial line. A segment of the epitaxial line between the two phases is shown to be inherently unstable, so unique meaning can be given to designating a structure as strained fcc Ti. The bulk structure of a film of Ti on Al{001} is shown to be strained fcc Ti, a new phase not on the phase diagram.

1. Introduction

One modern technique for producing metastable phases is to grow a film in pseudomorphic or coherent epitaxy on a substrate that has a surface mesh close to the surface mesh of the metastable phase [1]. The bonding of film to substrate is assumed to be strong enough in pseudomorphic epitaxy to strain the film mesh to the substrate mesh. Frequently, the film is thick enough, say eight or ten atomic layers, to have several interior layers with the bulk spacing. The atomic structure of that specimen, which includes the bulk layer spacing, can then be determined by quantitative low-energy electron diffraction (QLEED). Usually the film is strained because the mesh of the surface plane of the substrate does not match precisely a mesh in a plane of the metastable phase.

In order to claim that the measured strained structure is a strained specimen of a particular stable or metastable equilibrium phase of the film material, we usually show that a physically reasonable epitaxial strain, i.e., a strain in the two dimensions of the surface plane that is not larger than a few per cent, acting on that equilibrium phase can produce the observed structure. However, even if that strain calculation can be done, which requires knowledge of the elastic moduli of the equilibrium phase, there is still a conceptual difficulty in identifying a particular equilibrium phase as the one that is strained. Namely, we can ask why the observed structure cannot be regarded as a strained form of some other equilibrium phase, especially if the strains from several equilibrium phases are comparable. One object of the present work is to show that modern electronic theory can give a sharp criterion for this identification. The argument will be illustrated by showing that a film of Ti on Al{001} is strained fcc Ti. A second object is to estimate the limits of epitaxial strain that a phase can accept before it goes unstable.

The key to the unique identification is the capacity of modern electronic structure programs to calculate ground-state energies of arbitrary structures, including highly strained structures of the various equilibrium phases, with good accuracy. The strained structure can even be unstable. This capacity is exploited here for bct Ti, where a particularly convenient representation of the energy of bct Ti as a function of lattice constants a and c has recently been published [2], and a structure has been determined for epitaxial Ti on Al{001} by QLEED [3]. The work here verifies and enhances the previous structure determination, which depended on the assumption that the elasticity was linear up to the strained structure, i.e., that the strain could be treated as a small deformation of a cubic structure with constant elastic moduli. In the present work, the elastic moduli and the structure change substantially as the deformation proceeds, but the stresses and the elastic moduli can be calculated for all deformations.

2. Formulation and results

In reference [2] the total energy of tetragonal Ti (and six other metals) is calculated from first principles by the full-potential linearized-augmented plane-wave method using the code WIEN95 and the local-density approximation. The total energy per atom is represented by a power series in the tetragonal structural parameters c/a and V, the volume per atom. The power series has 28 terms and gives the energy per atom E to an accuracy better than 0.01 mRyd within the ranges $0.8 \leqslant c/a \leqslant 1.6$ and 100 au $(14.8 \text{ Å}^3) \leqslant V \leqslant$ 117 au (17.3 Å^3), which includes the three stationary points of E.

This simple analytic representation of the tetragonal energy $E(a, c)$ as a power series permits quick evaluation of E and its first and second partial derivatives from the power series for each derivative. Hence the stationary points of $E(a, c)$ corresponding to minima and saddle points of E are readily found from vanishing of first derivatives, and the elastic moduli from evaluation of second derivatives.

The quantity of greatest immediate interest for epitaxially strained states is the epitaxial line, i.e., the line of states for which $(\partial E/\partial c)_a = 0$, which is the epitaxial boundary condition of zero normal stress on the (001) plane. The epitaxial line is found by calculating E as a function of c at each a, and finding the c at which E is a minimum. The values of $(\partial E/\partial a)_c$ along the epitaxial line are also tabulated. The stationary points of E are the points on the epitaxial line at which $(\partial E/\partial a)_c$ also vanishes, and are then easily and accurately found by interpolation of the tabulated values. For Ti and in general, there are three stationary points of E, two minima and a saddle point, two of which must occur at the cubic structures $c/a = 1$ and $c/a = \sqrt{2}$ (since $(\partial E/\partial a)_c = (\partial E/\partial c)_a$ at cubic points).

Along the epitaxial line the isotropic in-plane stress is found from

$$\sigma = \frac{a}{2V} \left(\frac{\partial E}{\partial a} \right)_c \tag{1}$$

where the factor 1/2 occurs because both dimensions of the cross section change when a changes. Tetragonal elastic stiffness coefficients are conveniently defined by

$$\begin{aligned}
\bar{c}_{11} &= \frac{a^2}{V} \frac{\partial^2 E}{\partial a^2} \\
\bar{c}_{13} &= \frac{ac}{V} \frac{\partial^2 E}{\partial a\, \partial c} \\
\bar{c}_{33} &= \frac{a^2}{V} \frac{\partial^2 E}{\partial c^2}
\end{aligned} \tag{2}$$

which give the coefficients of the second-order differential of E in the Taylor expansion of E at point (a, c), namely,

$$\frac{\delta^2 E}{V} = \frac{\bar{c}_{11}}{2}\left(\frac{\delta a}{a}\right)^2 + \bar{c}_{13}\left(\frac{\delta a}{a}\right)\left(\frac{\delta c}{c}\right) + \frac{\bar{c}_{33}}{2}\left(\frac{\delta c}{c}\right)^2. \qquad (3)$$

These tetragonal elastic stiffness coefficients are related to the usual two-index elastic stiffness coefficients c_{ij} of the tetragonal structure by

$$\begin{aligned}
\bar{c}_{11} &= 2(c_{11} + c_{12}) \\
\bar{c}_{13} &= 2c_{13} \\
\bar{c}_{33} &= c_{33}.
\end{aligned} \qquad (4)$$

The relations (4) follow immediately by comparing the second derivatives of E in (2) with the second derivatives of E with respect either to a_1 or to a_1 and c of three orthogonal coordinates a_1, a_2, and c at $a_1 = a_2 = a$; such derivatives define the c_{ij}. The definitions (2) and relations (4) also appear and are discussed in [4]. The condition that $\delta^2 E > 0$ for all δa and δc, i.e., that $\delta^2 E$ is positive definite, is then

$$D \equiv \bar{c}_{11}\bar{c}_{33} - \bar{c}_{13}^2 > 0. \qquad (5)$$

Then when the stability index $D < 0$, there are strains for which $\delta^2 E < 0$ and the state is inherently unstable.

Plotted as functions of c/a along the epitaxial line of Ti in figures 1 and 2 are six quantities: the position of the epitaxial line on the tetragonal plane (coordinates c/a and V/V_0) and quantitative values of E, $\bar{c}_{ij}$, D, σ, and the strain $\delta a/a$ on each phase.

3. Discussion

The principal results of this work are, first, to establish that the strained epitaxial film of Ti on Al{001} can be uniquely identified as a strained specimen of the fcc phase of Ti, and, second, to evaluate the limits to the compressive strain and the tensile strain that the fcc phase can accept, beyond which the phase is inherently unstable.

The identification of the observed bulk structure of the Ti film as strained fcc Ti is shown in figures 1(a) and 2(a). In figure 1(a) the measured structure (open square) and its error line agree with the fcc segment of the epitaxial line around $c/a = \sqrt{2}$ and not with the segment around the bct phase at $c/a = 0.85$. In figure 2(a) the presence of an inherently unstable section separating the fcc from the bct segment is shown where $D < 0$. This phase identification is particularly interesting because fcc Ti does not appear on the usual pressure–temperature phase diagram, whereas bcc Ti occurs above 1155 K at zero pressure and above. At low temperatures, however, the bcc structure is unstable, but the nearby bct phase is metastable.

The position of the QLEED structure and error line in figure 1(a) uses the values $c = 4.28 \pm 0.06$ Å, $a = 2.8635$ Å from [3]. The a-value is the side of the unit-square surface mesh of Al{001}. The theoretical value of a for fcc Al is 2.84 Å, for the fcc phase of Ti it is 2.84 Å, and for the bct phase of Ti it is 4.48 Å. Thus fcc Ti is expected to be a very good match to a substrate of Al{001}; figures 1(a) and 2(c) indicate that the Ti lattice constant is compressed by 2.5% by the Al{001} substrate, and the experimental value of a for Ti is about 2.93 Å, as found in [3]. Although the theoretical a- and c-values are each 2–3% smaller than the experimental values, the theoretical reduced quantity c/a will be closer to the experimental value. The experimental value $c/a = 1.495$ clearly belongs to the fcc segment of the epitaxial line, and is far from the bct segment around $c/a = 0.85$.
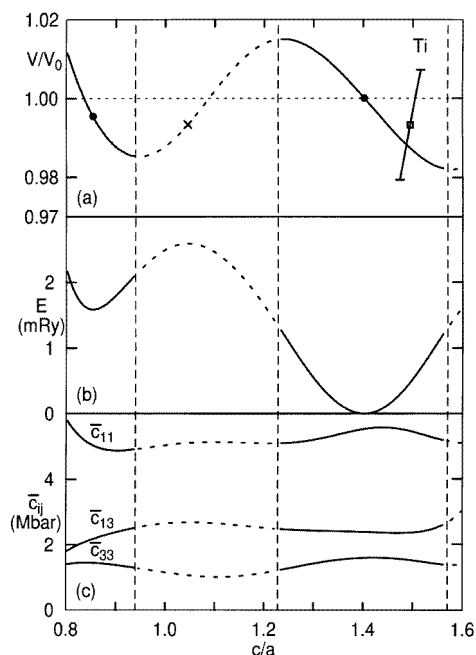
Figure 1. The epitaxial line for Ti on the tetragonal plane, coordinates c/a and V/V_0, where the reference volume $V_0 = 107.9$ au (16.0 Å^3) is the theoretical volume per atom of the equilibrium fcc Ti phase at $c/a = 1.40$. The fcc phase and the bct phase at $c/a = 0.85$ are marked by dots, and the saddle point at $c/a = 1.05$ by a ×. (The value of c/a is not exactly 1.00 or 1.41 at cubic points because of inaccuracy in the representation of the energy.) The LEED structure for a film of Ti on Al{001} [3] is marked by an open square at $c/a = 1.495$ and an error line arising from the error in c. V^{film} is reduced by dividing by the experimental volume $V_0^{exp} = 119.2$ au (17.7 Å^3) from the measured equilibrium structure of hcp Ti. The dashed sections of the epitaxial line between the dashed vertical lines and beyond the vertical line at $c/a = 1.57$ are unstable. (b) The energy per atom in mRyd along the epitaxial line, referred to zero at the equilibrium fcc phase. There are minima at the bct and fcc phase points and a maximum at the saddle point. (c) The tetragonal elastic stiffness coefficients $\bar{c}_{ij}$ in Mbar from equation (2) as functions of c/a along the epitaxial line.

In placing the LEED structure point in figure 1(a), the reduced volume V/V_0 is used for the ordinate. Again, as in the case of c/a, the *reduced* volume using the experimental value of V_0 will be closer to theory. Since measurements on equilibrium fcc Ti are not available, the value for hcp Ti is a reasonable estimate, and hence figure 1(a) uses $V_0^{hcp} = 119.2$ au (17.7 Å^3), which is about 10% greater than the theoretical value $V_0^{theor} = 107.9$ au (16.0 Å^3); some idea of the accuracy of using the hcp value of V_0 is shown by the case of Co, where both fcc and hcp phases are available—the volume per atom of hcp Co is 0.2% smaller than the volume per atom of fcc Co.

To exclude the interpretation of the measured strained film on Al{001} as strained hcp phase produced by anisotropic epitaxial strain, we need to apply again the idea that strained regions of each phase are separated by inherently unstable states on any continuous path between the phases, as is the case for tetragonal paths between the fcc and bct phases. Although the stability along hcp to fcc paths has not been calculated, the existence of an inherently unstable segment is very plausible, since any such path must go through points, such as saddle points, where curvatures of opposite sign in orthogonal directions will make
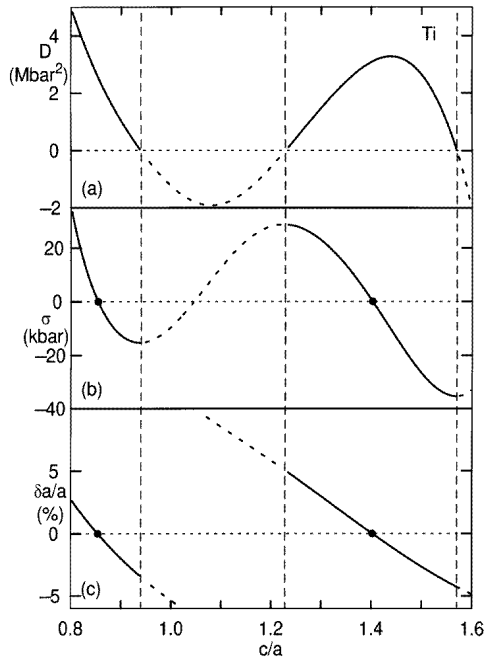
Figure 2. The stability index $D \equiv \bar{c}_{11}\bar{c}_{33} - \bar{c}_{13}^{2}$ versus c/a for Ti along the epitaxial line. The unstable section of the line where $D < 0$ is dashed and lies between $c/a = 0.94$ and 1.23. (b) The isotropic epitaxial stress σ in the (001) plane in kbar along the epitaxial line. The phase points are marked by dots. The unstable sections are dashed. (c) The isotropic epitaxial strain $\delta a/a$ in the (001) plane in % corresponding to the stress in figure 2(b) at each of the two phases. The bct phase is compressed by 3.4% and the fcc phase is expanded by 4.9% at the edges of the unstable section.

a stability index like D in (5) negative.

The second principal result is obtained from figures 2(a) and 2(c). Figure 2(a) shows that the fcc phase becomes inherently unstable for c/a below 1.23 and above 1.57. At these values of c/a figure 2(c) shows that 4.9% tensile epitaxial strain or 4.2% compressive epitaxial strain are the limits of strain accepted by the fcc phase. These strain limits are considerably smaller than the stability limit under hydrostatic tensile strain, which drives the bulk modulus to zero only after lattice expansions of greater than 30% [5]. From figure 2(b) the maximum epitaxial stresses that drive the fcc phase and the bct phase to instability are respectively 29 kbar of tension or 15 kbar of compression. These have both been reduced by nonlinear effects; thus if the Poisson ratio of fcc Ti remained constant at 0.43, the tensile stress at $c/a = 1.23$ would be 48 kbar.

Note that E plotted in figure 1(b) along the epitaxial path is the lowest energy along any path in the tetragonal plane between the minima at the two phases, and has a maximum of 2.59 mRyd at the saddle point at $c/a = 1.05$. It is noteworthy that the c_{ij} in figure 1(c) show strong nonlinearity, but no special behaviour at the stability limits $c/a = 0.94$ and 1.23. The special behaviour is shown by the vanishing of D in figure 2(a), which corresponds to $\delta^{2}E = 0$ when $\epsilon_{3}/\epsilon_{1} = -\bar{c}_{13}/\bar{c}_{33} = -\bar{c}_{11}/\bar{c}_{13} = -1.95$ at $c/a = 0.94$ and -2.05 at $c/a = 1.23$. The strained bct structure is weakest for these strain ratios.

In summary, these first-principles calculations allow us to draw conclusions about the existence of tetragonal equilibrium phases and the range of stability of epitaxial strain on

these phases. Although there is limit on the accuracy of the calculations, that limit is known, is plausibly about the same for stable and unstable states, and is made smaller by comparison of reduced experimental quantities with theory. The main conclusions should therefore be reliable.

Acknowledgments

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