



Strain-induced change in the elastically soft direction of epitaxially grown face-centered-cubic metals

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The theory of epitaxial strain energy is extended beyond the harmonic approximation to account for large film/substrate lattice mismatch. We find that for fcc noble metals ~i! directions $\langle 001 \rangle$ and $\langle 111 \rangle$ soften under *tensile* biaxial strain ~unlike zincblende semiconductors! while ~ii! $\langle 110 \rangle$ and $\langle 201 \rangle$ soften under *compressive* biaxial strain. Consequently, ~iii! upon sufficient compression $\langle 201 \rangle$ becomes the softest direction ~lowest elastic energy!, but ~iv! $\langle 110 \rangle$ is the hardest direction for large tensile strain. ~v! The dramatic softening of $\langle 001 \rangle$ in fcc noble metals upon biaxial tensile strain is caused by small fcc/bcc energy differences for these materials. These results can be used in selecting the substrate orientation for effective epitaxial growth of pure elements and $A_p B_q$ superlattices, as well as to explain the shapes of coherent precipitates in phase separating alloys. © 1998 American Institute of Physics. ©S0003-6951-98!00204-6#

When a material is compressed *hydrostatically*, its energy rises steeply because all three crystal axes are deformed ~dashed line in Fig. 1!. When the same material is confined coherently onto a substrate ~“coherent *epitaxy*”! with lattice constant a_s , the energy rises less steeply ~solid line in Fig. 1! since it is deformed only along the crystal axes in the substrate plane and allowed to relax ~and thus, lower its energy! in the third direction \hat{G} . This “epitaxial softening” can be quantified by the dimensionless parameter

$$q_{a_s, \hat{G}} \approx \frac{DE^{\text{epi}}_{a_s, \hat{G}}}{DE^{\text{bulk}}_{a_s}}, \quad \sim 1! \quad (1)$$

giving the ratio between the epitaxial increase in energy due to biaxial deformation to a_s , and the hydrostatic increase in energy due to triaxial deformation to the same a_s . Because

indicate when and how expression ~2! will fail for a given system. Figure 1 shows that at least a fourth-order polynomial in a_s is needed to reproduce the qualitative structure in $DE^{\text{epi}}(a_s, @001\#)$ for Cu, as obtained directly from accurate electronic structure calculations ~see below!. The three extremal points in $DE^{\text{epi}}(a_s$

deviates from a_{eq} . This is apparent from the dependence of q on a_s absent in the harmonic theory!, from the crossing of q for different \hat{G} values, and from the development of new lobes and minima in Fig. 2 with the change in a_s . Such effects occur at $\Delta a/a$, 4%, suggesting a rather small range of validity of the harmonic approximation. Furthermore, in the harmonic elasticity theory, if $\langle 001 \rangle$ is the softest direction then $\langle 111 \rangle$ must be the hardest direction, and vice versa. Figure 3 shows that this does not hold for sufficiently deformed films: the hardest direction in Ni and Cu for $a_s @ a_{eq}$ is $\langle 201 \rangle$ while the hardest directions for Ag and Au at $a_s @ a_{eq}$ are $\langle 111 \rangle$ and $\langle 001 \rangle$.

The new results for fcc noble metals, apparent from our self-consistent LDA calculations, are:

- i! $q(a_s, \langle 001 \rangle)$ and, to a lesser extent, $q(a_s, \langle 111 \rangle)$ soften as a_s expands tensile biaxial strain!
- ii! $q(a_s, \langle 110 \rangle)$ and $q(a_s, \langle 201 \rangle)$ soften as a_s is compressed.
- iii! As a result of -i! and -ii! above, we find that upon sufficient compression, $\langle 001 \rangle$ is no longer the elastically softest direction but $\langle 201 \rangle$ and to a lesser extent $\langle 110 \rangle$ are. The hardest direction upon compression is still $\langle 111 \rangle$.
- iv! Upon sufficient expansion, $\langle 111 \rangle$ is no longer the hardest direction, but $\langle 110 \rangle$ is -Cu, Ni!. The softest direction upon expansion is still $\langle 001 \rangle$.

We find that result -i! is a reflection of the existence of a low-energy bcc and bct ‘‘excited’’ structures. Indeed, $\langle 001 \rangle$ strain applied to fcc lattice defines a Bain path,¹³ transforming fcc into bcc via the body-centered tetragonal structure. This intermediate structure is characterized by tetragonal unit cell dimensions a and c . When minimizing the total energy of a $\langle 001 \rangle$ biaxially deformed solid with respect to the out-of-plane lattice vector c at each in-plane lattice parameter a_s , one finds an ‘‘epitaxial $\langle 001 \rangle$ Bain path’’,¹⁴ solid line in Fig. 1!. For noble metals having the fcc structure ($c/a \approx \sqrt{2}$) at equilibrium, this deformation path contains the bcc ($c/a \approx 1$) saddle point, and the bct ($c/a \approx 0.96$ in the case of Cu) local minimum.^{14–16} The low amplitude of the epitaxial $\langle 001 \rangle$ Bain path relative to the hydrostatic path -Fig. 1! defines the softness of $q(a_s, \langle 001 \rangle)$ via Eq. -i!, and therefore is a direct manifestation of the small fcc/bcc and fcc/bct energy differences. Indeed, the epitaxial softening function at $c/a \approx 1$ is given by

$$q(a_s, \langle 001 \rangle) \approx \frac{DE^{bcc/fcc}}{DE_{fcc}^{bulk} a_s}, \quad -5!$$

where $DE^{bcc/fcc} \approx E_{tot}^{bcc}(V_{eq}^{bcc}) - E_{tot}^{fcc}(V_{eq}^{fcc})$. Since in fcc noble metals $V_{eq}^{bcc} < V_{eq}^{fcc}$, the bcc point is reached at