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

V. Ozoliņš,[a] C. Wolverton, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

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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 ^001& and ^111& soften under *tensile* biaxial strain ~unlike zincblende semiconductors! while ~ii! ^110& and ^201& soften under *compressive* biaxial strain. Consequently, ~iii! upon sufficient compression ^201& becomes the softest direction ~lowest elastic energy!, but ~iv! ^110& is the hardest direction for large tensile strain. ~v! The dramatic softening of ^001& 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_pB_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

$$q\sim a_s,\hat{G}!\ 5\ \frac{\mathrm{D}E^{\mathrm{epi}}\sim a_s,\hat{G}!}{\mathrm{D}E^{\mathrm{bulk}}\sim a_s!}, \qquad \sim 1!$$

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 D$E^{\mathrm{epi}}(a_s,$@001#) for Cu, as obtained directly from accurate electronic structure calculations ~see below!. The three extremal points in D$E^{\mathrm{epi}}(a_s$

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 $\mathrm{D}a/a$, 4%, suggesting a rather small range of validity of the harmonic approximation. Furthermore, in the harmonic elasticity theory, if ^001& is the softest direction then ^111& 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 ^201&, while the hardest directions for Ag and Au at a_s ! a_{eq} are ^111& and ^001&.

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

~i! $q(a_s,@001\#)$ and, to a lesser extent, $q(a_s,@111\#)$ soften as a_s *expands* ~tensile biaxial strain!.

~ii! $q(a_s,@110\#)$ and $q(a_s,@201\#)$ soften as a_s is *compressed.*

~iii! As a result of ~i! and ~ii! above, we find that upon sufficient compression, ^001& is no longer the elastically softest direction but ^201& and to a lesser extent ^110& are. The hardest direction upon compression is still ^111&.

~iv! Upon sufficient expansion, ^111& is no longer the hardest direction, but ^110& is ~Cu, Ni!. The softest direction upon expansion is still ^001&.

We find that result ~i! is a reflection of the existence of a *low-energy* bcc and bct ''excited'' structures. Indeed, ^001& 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 ^001& 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 ^001& Bain path''[14] ~solid line in Fig. 1!. For noble metals having the fcc structure (c/a 5 $\mathrm{A}\overline{2}$) at equilibrium, this deformation path contains the bcc (c/a 5 1) saddle point, and the bct (c/a 5 0.96 in the case of Cu! local minimum.[14–16] The low amplitude of the epitaxial ^001& Bain path relative to the hydrostatic path ~Fig. 1! defines the softness of $q(a_s,@001\#)$ via Eq. ~1!, and therefore is a direct manifestation of the small fcc/bcc and fcc/bct energy differences. Indeed, the epitaxial softening function at c/a 5 1 is given by

$$q\sim a_s,@001\#!\ 5\ \frac{\mathrm{D}E^{\mathrm{bcc/fcc}}}{\mathrm{D}E^{\mathrm{bulk}}_{\mathrm{fcc}}\sim a_s!},\qquad \sim 5!$$

where $\mathrm{D}E^{\mathrm{bcc/fcc}}\ 5\ E^{\mathrm{bcc}}_{\mathrm{tot}}(V^{\mathrm{bcc}}_{\mathrm{eq}})\ 2\ E^{\mathrm{fcc}}_{\mathrm{tot}}(V^{\mathrm{fcc}}_{\mathrm{eq}})$. Since in fcc noble metals $V^{\mathrm{bcc}}_{\mathrm{eq}}$ ' $V^{\mathrm{fcc}}_{\mathrm{eq}}$, the bcc point is reached at