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Interplay between misfit strain relief and Stranski–Krastanov growth in fcc (111)/bcc (110) ultrathin film epitaxy

Part 1. Analytical approach

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Abstract

The main objective of this investigation is to study the impact of misfit (homogeneous) strain (MS) relief by misfit dislocations (MDs) — or a misfit vernier where the relaxation into oscillatory strains characteristic of MDs becomes insignificant — on the Stranski–Krastanov (SK) growth mode, the perception being that the driving force for the transition is dominated by short range proximity effects of the vacuum and a strongly bonding substrate. The influence of misfit strain relief with increasing thickness on the transition from two-dimensional (2D) to three-dimensional (3D) growth, characteristic for SK growth, is investigated. Here, the dominating parameters are identified and the mathematical formulae for the governing relations, needed for quantification in Part 2, using embedded atom methods (EAM) potentials, are derived: (i) the dependence of substrate coverage on epilayer misfit (f) and deformation ($\bar{e}$); (ii) the structure of Fourier series to model fcc (111) epilayer–bcc (110) substrate interaction potentials $V(x, y)$ for a Kurdjumov–Sachs (KS) orientation, including optimum Fourier coefficients V_{hk} for low order truncations; (iii) the harmonic intra-epilayer interaction suitable to describe MDs and to model misfit vernier accommodation of mismatch related to homogeneous Poisson strain; (iv) the average in-plane strain energy suitable (a) to handle the large repeat periods involved in homogenous epilayer deformation within the short wavelength periodic epilayer–substrate interaction potentials and (b) to define stiffness constants for epilayer deformation within such a field; (v) stability criteria for MS relief of 2D coherent and one-dimensional (1D) KS coherent — registry of two opposing sets of parallel closest packed atom rows on either side of the interface — epilayers in Nishiyama–Wassermann and KS orientations, respectively, applying continuum and discrete approaches; and (vi) criteria for growth mode realization, emphasizing transitions to the SK mode and its dependence on proximity effects. The analytical considerations reveal (a) that the transition from a 2D coherent misfit accommodation mode to a 1D KS mode is favored by a large excess strain energy $\epsilon_{2D}-\epsilon_{1D}$ and large substrate surface free energy, but opposed by strong epilayer–substrate *bonding* and (b) the MS energy ϵ makes no contribution to the growth mode discriminant if proximity effects of the interface and free surface are absent. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is of great technological and fundamental interest to grow thin films of uniform thickness with atomically smooth surfaces and perfect crystallinity. Such films are most efficiently produced by epitaxial growth. The former characteristic is best served by growing in the monolayer-by-monolayer (ML-by-ML) mode. Bauer [1] has identified three major growth modes: island growth, also referred to as Volmer–Weber (VW) or three-dimensional (3D) growth; ML-by-ML growth, also referred to as Frank–van der Merwe (FM) or two-dimensional (2D) growth; and Stranski–Krastanov (SK) growth, in which the growth continues in VW mode after completion of one or a few MLs in 2D mode. The equilibrium criteria

$$\Delta\gamma=\gamma_0+\gamma_{\rm i}-\gamma_{\rm s}\leq 0 \text{ for FM and SK}$$

$$\Delta\gamma=\gamma_0+\gamma_{\rm i}-\gamma_{\rm s}>0 \text{ for VW} \tag{1a}$$

for the realization of specific growth modes, proposed by Bauer, have become generally accepted. In Eq. (1a) γ_0, $\gamma_{\rm i}$ and $\gamma_{\rm s}$ are, respectively, the specific surface free energies of the overlayer (epilayer), overlayer–substrate interface and the substrate. Bauer and van der Merwe [2] have proposed that in many material combinations the interfacial energy $\gamma_{\rm i}$ makes a negligible contribution to the value of $\Delta\gamma$, so that the difference $\gamma_0-\gamma_{\rm s}$ provides a rule-of-thumb criterion for the prediction of different growth modes. The present approach also lends itself to simply testing the validity of the proposal of Bauer and van der Merwe [2].

In practice, the change from 2D to SK growth seems to be the rule rather than the exception [3,4]. It thus comes as no surprise that this phenomenon, that will also be a major issue here, has recently been the subject of intensive study. Various models — we believe more or less complimentary — have been proposed to explain this phenomenon. The present study follows Matthews' [5] suggestion that the introduction of misfit dislocations (MDs) at the epilayer–substrate interface, above the critical thickness $h_{\rm c}$, where a pseudomorphic epilayer is unstable, may facilitate the transition from 2D to 3D growth. The argument is that the net energy change — increase of the interfacial energy $\gamma_{\rm i}$ by the presence of the MDs and the decrease of strain energy in the epilayer — effects a transition of $\Delta\gamma$ from the negative to the positive domain [6,7].

One can look at the change of $\Delta\gamma$ with increasing thickness also from the point of view of bonding. Thermal desorption experiments clearly show that the bonding decreases rapidly with increasing thickness until the bonding between the deposited atoms becomes stronger than that to the underlayer, causing the formation of 3D crystals. This substrate proximity effect is supported by embedded atom method (EAM) calculations [7]. Multilayer relaxation constitutes an important mechanism by which the range of interface proximity effects is extended and interlayer bonding modified.

Following Bauer [1] we adopt the criterion that the sign of the growth mode discriminant $\Delta E_{n+1,n}$, that is, the energetic change of an epilayer–substrate system, when we transfer material from the ML at the top, the $(n+1)$th ML, to the nth one, determines the energetic tendency of the nth layer to pursue a given growth mode. If follows that [7]

$$\Delta E_{n+1,n}=2E_n-E_{n+1}-E_{n-1}<0;\ \text{2D growth}$$

$$\Delta E_{n+1,n}=2E_n-E_{n+1}-E_{n-1}>0;\ \text{VW growth.} \tag{1b}$$

In Eq. (1b) E_n is, for example, the EAM calculated energy per unit interfacial area for the section of the system in which the epilayer is n layers thick. When $\Delta E_{n+1,n}<0$ it is energetically favorable for the nth ML to cover up the $(n-1)$th ML, i.e. to favor 2D growth. 3D (VW) growth is favored when $\Delta E_{n+1,n}>0$. A sign change of the discriminant at $n\geq 2$ marks the onset of 3D growth, characteristic of SK growth. When $n=1$ the $E_0=\gamma_{\rm s}$ and the relation (1b) reduces to (1a).

It has also been suggested [8] that the transition from the 2D layer to 3D islands with MD formation can occur via 3D islands coherent with the substrate, the strain in the islands being released by strain relaxation between the islands; the claim being that the gain in energy due to strain relaxation exceeds the energy increase due to the strain and increased surface area by island formation. Clearly the misfit strain, misfit dislocation and specific surface free energies have interdependent effects on growth modes. All these properties are also strongly dependent on film thickness, i.e. proximity effects from the substrate and vacuum.

In this investigation we wish to study the dependence of certain properties of a fcc {111} epilayer growing under quasi-equilibrium conditions either directly in Kurdjumov–Sachs (KS) orientation on a {110} bcc substrate or by misfit strain (MS) relief (i) from 2D coherence to the KS orientation with one-dimensional (1D) coherence (1D KS) and (ii) from this configuration to KS with MDs on misfit (f), bonding (γ) and thickness h, measuring h in terms of number of layers (n). These properties are: (a) the strain energy and elastic constants; (b) the resistance against MS relief by the introduction of MDs; and (c) its tendency for a change from 2D to SK growth. In Part 2 the atomic interactions will be modeled by EAM potentials. We take the specific surface free energy γ — defined as half of the work per unit area to separate a crystal into two halves — as an appropriate measure of bond strength *within* the film and *within* the substrate. Our bias for the KS orientation is motivated by the fact that it is of common occurrence and reduces the problem approximately to a 1D one [9]. Furthermore, since 1D coherence (registry in y-direction) in KS orientation implies a misfit in the x-direction, large enough to be accommodated by a misfit vernier (MV), in this paper ID KS$\equiv$(reg.-y, MV-x).

While it is true that the growth mode may be influenced by many other factors, e.g. non-equilibrium conditions and impurities, this investigation is restricted to pure crystals growing under quasi-equilibrium conditions, the supposition being that useful guidelines may emanate from such a study.

Previously [10] it has been shown, using EAM, that the stiffness constants c_{ij} of epitaxial {111} MLs of Cu and Ni on a W{110} substrate, for which the epilayer–W interaction energy corrugations are smoothed by averaging, are only about 60% of what they are in the bulk, and that the stable structure of the epimonolayer on the smoothed substrate is expanded by about 2.5% compared with the bulk structure. This is a case in which the γ values [11] for Cu and Ni, 1.934 and 2.364 J/m^2, respectively are significantly less than that (3.468 J/m^2) of W. It has subsequently been shown [7] that in EAM modeling of atomic interaction the effect of substrate proximity vanishes after about 3 ML, but could extend more as a result of interlayer relaxation. Since stiffness constants are involved in calculating strain energy, proximity effects are expected to feature strongly in this study.

The effect of MS energy E_{MS} on the growth mode has also been addressed [7] in the case of Cu on W. In this case the transition to SK mode occurs at 2 ML thickness [3]. The calculations show that the main force driving the transition in this case emanates from the strongly bonding substrate. The calculations did not allow though for the instability of misfit accommodation by MS relief and the introduction of MDs; the epilayer has been taken to remain pseudomorphic.

In the present investigation we wish to extend the calculations in several aspects. Firstly we select a crystal combination in which the bonding (γ) in the substrate exceeds that in the epilayer somewhat, so that by Bauer's criteria [1,2] the system could possibly be a limiting case of SK growth. Secondly we also select the pair — fcc (111) on bcc (110) — such that the epilayer should prefer to grow in the KS orientation, shown in Fig. 1, either directly from the beginning or after a transition, involving a rotation, from 2D coherence in the Nishiyama–Wassermann (NW) orientation. Thirdly the selection is made such that 1D coherence exists — registry of two opposing *sets* of parallel closest packed atomic rows on either side of the interface ([$\bar{1}$11] bcc, [$\bar{1}$11] fcc), i.e. the misfit in KS orientation is below a critical value above which MDs would enter the ML–substrate interface and a critical layer thickness accordingly exists above which the 1D MS is relieved by MDs.

It has also previously [12] been shown that the KS orientation is energetically more favorable when the misfit between densely packed atomic rows on either side of the interface (see Fig. 1), i.e.

$$f_{\mathrm{KS}}=\frac{d_b-d_a}{d_a}=\frac{r}{r_{\mathrm{KS}}}-1, \qquad (2)$$

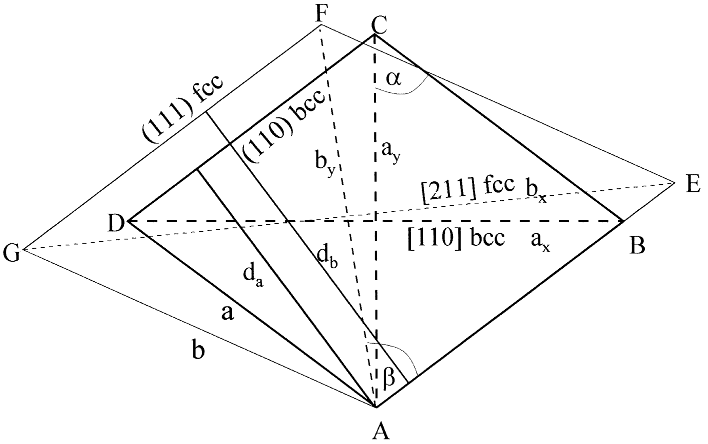

Fig. 1. An illustration of a fcc (111) surface unit cell AEFG in Kurdjumov–Sachs (KS) orientation on a bcc (110) surface unit cell ABCD. The KS epitaxial orientation is obtained when the spacings d_a and d_b of the densest packed atomic rows in the two crystals are either equal or closely similar. The nearest neighbor distances a and b and the rhombic angles α and β are given in Eq. (3).

$$d_a = a \sin 2\alpha, \quad d_b = b \sin 2\beta; \quad \tan \alpha = \sqrt{2},$$
$$\beta = \pi/3; \quad r = b/a, \quad r_{KS} = (32/27)^{1/2} = 1.0887 \qquad (3)$$

is small enough, b and a being the nearest neighbor distances in the fcc {111} epilayer and the bcc (110) substrate, respectively. When f_{KS} deviates from zero the NW orientation becomes favorable at a deviation depending on the ratio of intralayer to interfacial bondings. The 2D coherent configuration may even be energetically favorable if the epilayer is thin enough.

The possibility that at ML coverage Cu could grow completely (2D) coherently is a real one. Cu does so on W{110} [3]. While it is true that the bondings within the W substrate ($\gamma \equiv 3.468$ J/m^2) and within the Cu–W interface are significantly stronger than within an Fe substrate and Cu–Fe interface, for example, it is also true that the ratio $r = b/a (\approx 1.03)$ for the Cu–Fe interface is very close to the value 1.04 where the tendency to 2D coherence is optimum [12].

Let us accordingly assume that the first ML may grow fully 2D coherently and that at double layer (DL) thickness there occurs a transition to a configuration with a misfit vernier in the x-direction $[\bar{1}10]_{bcc}$ while 1D coherence is maintained in the y-direction $[001]_{bcc}$. Misfit accommodation in the x-direction by a misfit vernier is a fair approximation justified by the large misfit ($\sim$20%) in this direction [12]. While it is true that the misfit f, as defined by $f = (b - a)/a$, may be small for a given pair of atomic rows on either side of the interface, drastic disregistry will occur for neighboring pairs, because of the angular mismatch $\beta - \alpha$. For perfect 1D KS matching the 'effective' mismatch is estimated to be near 20%. The considerations in Appendix A support the contention that strong epilayer–substrate bonding is conducive to commencement of growth in the 2D coherent configuration as in the growth of Cu on W(110) [3], whereas large excess $\epsilon_{2D} - \epsilon_{1D}$ of MS energy between the 2D coherent (ϵ_{2D}) and 1D KS (ϵ_{1D}) configurations and large substrate surface free energy γ energetically favor commencement in the 1D KS configuration. It seems reasonable to assume that this will precede the transition which involves MDs in the y-direction rather than conservation of coherence. In order to study the effect of MS relief on a growth mode transition in the second layer itself, the growth conditions of the third layer will also be required.

While the investigation involving MDs is facilitated by applying the continuum elasticity theory of epitaxy for an 'infinite' interface, the investigation involving 2D registry or 1D registry in combination with a misfit vernier can be handled more basically in the discrete, i.e. atomic, approach, which has the merit of accounting for the surface free energy changes related to coverage changes of the substrate by epilayer deformation. This energy source has been ignored in the classical theory. Details of the discrete approach are given in Appendix B.

2. Geometry

For the calculation of the distribution of misfit accommodation between MS, misfit vernier and MDs in the KS orientation we need to construct geometrical relations between the relevant misfit f_{KS}, the MS $\bar{e}$ and the MD density $\bar{f}_{\text{KS}}$. A complication is that the equilibrium structure and stiffness of the supported film changes with thickness for small — about 1–4 ML — thicknesses because of substrate proximity effects [7,10]. For systems where the bondings are not significantly different, the effect is possibly small, but does not vanish since part of it stems from the fact that the epilayer deforms relative to a fixed interacting substrate.

Another geometrical factor of significance is the size of the system. In order to handle this feature for an ultrathin epilayer that relieves strain on a 'rigid' (thick) substrate, it is convenient to model the system in terms of a finite, e.g. rectangular, epilayer slab of uniform thickness on an extensive substrate. The application of physical principles is facilitated (a) by restricting the epilayer to a fixed number of atoms — a condition which is fully met for a given uniform thickness by a fixed number $N^{E_{\text{P}}}$ of interfacial epilayer atoms and (b) to account for the substrate size in terms of the number N^{S} of covered substrate surface atoms.

For convenience we modify the notation in Eq. (2) somewhat to reflect more appropriately the thickness dependence and the (x, y) axes introduced in Fig. 1; we replace the subscript SK by y and introduce a superscript (n) to reflect the effect of substrate proximity on the equilibrium structure of an epilayer comprising n layers. We introduce the notation $f_y^{(n)}$, $\bar{f}_y^{(n)}$ and $\bar{e}_y^{(n)}$, respectively, for the misfit, the misfit dislocation density and the misfit strain and wish to stress the significance of $\bar{f}_y^{(n)}$ as a measure of disregistry of a strained epilayer. These quantities are defined in terms of the unstrained $[b^{(n)}, d_b^{(n)}]$ and homogeneously strained $[\bar{b}^{(n)}, \bar{d}_b^{(n)}]$ values by the relations

$$d_b^{(n)} = d_a[1+f_y^{(n)}],\ \bar{d}_b^{(n)} = d_a[1+\bar{f}_y^{(n)}] = d_b^{(n)}[1+\bar{e}_y^{(n)}];\quad n=1,2,3. \tag{4a}$$

For mathematical convenience we also introduce the analogous relations

$$b^{(n)} = a[1+f_x^{(n)}],\ \bar{b}^{(n)} = a[1+\bar{f}_x^{(n)}] = b^{(n)}[1+\bar{e}_x^{(n)}] \tag{4b}$$

for the x-direction $[\bar{1}10]$ in Fig. 1. It is also of interest to know the degree to which the quantities $b^{(n)}$ and $d_b^{(n)}$ differ from their corresponding bulk values b^{∞} and d_b^{∞}. This may be conveniently expressed in terms of fictitious strains $\bar{e}_{\text{in}}$ as

$$d_b^{(n)} = d_b^{\infty}(1+\bar{e}_{yn}) \text{ and } b^{(n)} = b^{\infty}(1+\bar{e}_{xn}). \tag{4c}$$

Note that here $f_x^{(n)}$ and $\bar{f}_x^{(n)}$ do not carry the true meanings of misfit and misfit dislocation density, respectively. They are useful though in deriving a relation between the numbers of interfacial epilayer ($N^{E_{\text{P}}}$) and covered substrate surface (N^{S}) atoms. If the epilayer is rectangular with lateral dimensions $L_x \times L_y$ and $\bar{L}_x \times \bar{L}_y$ when unstrained and homogeneously strained, respectively, it follows that

$$N^{E_{\text{P}}} = L_x L_y / b^{(n)} d_b^{(n)} = \bar{L}_x \bar{L}_y / \bar{b}^{(n)} \bar{d}_b^{(n)},$$

$$N^{\text{S}}[f^{(n)}] = L_x L_y / a d_a,\ N^{\text{S}}[\bar{f}^{(n)}] = \bar{L}_x \bar{L}_y / a d_a \tag{5}$$

where $N^{\text{S}}[f^{(n)}]$ is the number of substrate atoms covered by the unstrained ($\bar{e}_i = 0$) epilayer and $b^{(n)} d_b^{(n)}$, $\bar{b}^{(n)} \bar{d}_b^{(n)}$ and $a d_a$ are the relevant areas per atom. On substituting from Eqs. (4a) and (4b) we obtain

$$N^{\text{S}}[f^{(n)}] = N^{E_{\text{P}}}[1+f_x^{(n)}][1+f_y^{(n)}],$$

$$N^{\text{S}}[\bar{f}^{(n)}] = N^{E_{\text{P}}}[1+\bar{f}_x^{(n)}][1+\bar{f}_y^{(n)}], \tag{6}$$

$$\bar{f}_i^{(n)} = f_i^{(n)} + [1+f_i^{(n)}]\bar{e}_i^{(n)};\ i = x, y. \tag{7}$$

We plan to calculate the growth mode discriminants for epilayers comprising sections with (i) 2D registry $[\bar{f}_x^{(n)} = \bar{f}_y^{(n)} = 0]$, (ii) 1D registry along y with a misfit vernier along x and (iii) MDs along y with misfit vernier along x to be designated respectively as (reg.-y, MV-x) and (MD-y, MV-x), where $\bar{e}$ denotes MS.

On using the Poisson ratio $\nu^{(n)}$ of Eq. (17) and

Eqs. (4) to (7), we may define the ratio

$$q^{(n)}(\bar{e}) \equiv N^{\mathrm{S}}(\bar{e})/N^{E_{\mathrm{P}}} = 1 \qquad \text{for } \bar{e} = \bar{e}_{2\mathrm{D}} \tag{8a}$$

$$= \frac{b^{(n)}}{a}\left\{1 - v^{(n)}\left[\frac{d_a}{d_b^{(n)}} - 1\right]\right\} \text{ for } \bar{e} = \bar{e}_{1\mathrm{D}}. \tag{8b}$$

If we assume that the deformation — MS relief — $\bar{e}_{2\mathrm{D}}$ to $\bar{e}_{1\mathrm{D}}$ involves *increased* substrate coverage, the number of substrate surface atoms that become covered in the transition from 2D registry to 1D registry and a misfit vernier is given by

$$\Delta N^{\mathrm{S}} \equiv N^{\mathrm{S}}(\bar{e}_{1\mathrm{D}}) - N^{\mathrm{S}}(\bar{e}_{2\mathrm{D}}) = N^{E_{\mathrm{P}}}[q^{(n)}(\bar{e}_{1\mathrm{D}}) - 1]. \tag{9}$$

It can be shown, using Eqs. (4)–(9), that the coverage increases for all positive values of $f_{\mathrm{KS}}(\equiv f_y)$ and for negative values satisfying the condition $|f_{\mathrm{KS}}| < (r_{\mathrm{KS}} - 1)/(1 + v)$, which is about 7% for realistic values of r_{KS} and v.

3. Energetics

3.1. Embedded atom method potentials

In EAM potentials, which we use for quantification, the total energy of an atomic arrangement with respect to the configuration of free stationary atoms is expressed as [13]

$$E = \frac{1}{2}\sum_{i \neq j} \phi(r_{ij}) + \sum_i F(\rho_i); \quad \rho_i = \sum_{j \neq i} f_j(r_{ij}) \tag{10}$$

where $\phi(r_{ij})$ is the pair potential energy of atoms i and j at separation r_{ij}, ρ_i may, for the present purpose, be interpreted as the total electron density at atom i due to all the other atoms j ($j \neq i$), each making a contribution $f_j(r_{ij})$ and that $F(\rho_i)$ is the energy involved in embedding atom i in the electron density ρ_i. Both ϕ and f are usually expressed in terms of polynomials and the limited ranges of atomic interaction (one or a few atomic diameters) built into them in terms of cutoff radii beyond which the corresponding quantity, ϕ or f, vanishes. We adopt the EAM developed by Johnson [14,15], the details of which are given elsewhere [7,16,17].

We may, instead of EAM energies, express the relevant quantities in terms of defect energies which differ from EAM energies by the cohesive energy. Because of the short range of atomic interaction, the defect energy has the apparent computational advantage of vanishing within a few atomic distances from a surface or interface.

3.2. Interfacial interaction: Fourier representations

As noted above, the calculation of the physical properties of an epilayer is — in the present approach — facilitated by representing the relevant periodic quantities in terms of Fourier series, which may usually be truncated at low order harmonics. EAM is used in Part 2 to quantify the optimum Fourier coefficients [16,18,19].

The Fourier representation $V(x', y')$ for the interaction energy (per interfacial epilayer atom) between an epilayer atom and a bcc (110) substrate is most simply written [10] by making use of the two-fold symmetry of the $(x', y') \equiv ([\bar{1}10], [001])$ axes. The second order truncation

$$V^{(2)}(x', y') = 2V_{00} + \sum_{h+k=2} V_{hk}\left\{\cos\left[2\pi\left(\frac{hx'}{a_x} + \frac{ky'}{a_y}\right)\right] + \cos\left[2\pi\left(\frac{hx'}{a_x} - \frac{ky'}{a_y}\right)\right]\right\};$$

$$a_x = 2a\sin\alpha,\ a_y = 2a\cos\alpha \tag{11a}$$

is usually adequate [12] for the description of the NW and KS orientations; a_x and a_y being the diagonal lengths of the rhombic bcc (110) unit cell in Fig. 1.

The description of the KS orientation is facilitated by a rotation θ of substrate axes which aligns the x-axis along bcc $[\bar{1}11]$. The relation between the (x', y') and (x, y) axes is given by

$$x' = x\cos\theta - y\sin\theta, \quad y' = x\sin\theta + y\cos\theta,$$

$$\theta = \pi/2 - \alpha. \tag{11b}$$

When substituted into Eq. (11a) this yields the result

$$V^{(2)}(x,y)=2V_{00}+2V_{20}\cos\left[4\pi\left(\frac{x\sin\alpha-y\cos\alpha}{2a\sin\alpha}\right)\right]+2V_{02}\cos\left[4\pi\left(\frac{x\cos\alpha+y\sin\alpha}{2a\cos\alpha}\right)\right]+V_{11}\left\{\cos\left[2\pi\left(\frac{x\sin2\alpha-y\cos2\alpha}{d_a}\right)\right]+\cos\left(\frac{2\pi y}{d_a}\right)\right\}. \quad (11c)$$

When we calculate average energies, the terms with non-vanishing arguments in x vanish in averaging [10] along x because of the misfit vernier in the x-direction — manifested by Eq. (17) and justified by the large 'effective' misfit, near to 20%. The constant and the term in y only, i.e. [9]

$$V^{(2)}(y;H)=2V_{00}(H)+V_{11}(H)\cos\left(\frac{2\pi y}{d_a}\right);\quad H=\langle H^{e}\rangle \quad (11d)$$

remain to determine the energetics of the atoms in the ML at an average equilibrium 'height' H above the substrate.

The optimization [18] of the Fourier coefficients V_{hk} for the truncation to most accurately map the epilayer–substrate interaction involves the computation of energy. To compute the energy of an epilayer on a semi-infinite substrate, one is faced with two dimensional issues: (i) if the arrangement of atoms on either side of the interface does not match the repeat period, then the lateral dimensions involved could be immense; and (ii) for a semi-infinite substrate an 'infinite' number of atomic layers need to be accounted for — clearly problematic computational goals. Issue (i) is resolved by homogeneously deforming the epilayer into interfacial matching, a configuration in which the repeat period is reduced to just one substrate surface unit cell. The role of the resulting strain energy will be considered below. Issue (ii) is resolved by involving only substrate layers that are non-negligibly influenced by the proximity of the interface.

The optimization of the coefficients V_{hk} of the truncation $V^{(2)}(x,y)$ involves K^2 EAM calculated energy differences E_{ij} per interfacial epilayer atom of the epilayer–substrate system (the *epilayer being uniformly deformed into registry dimensions*) and the two separated crystals; the interlayer spacings being varied so as to minimize E_{ij}, where K^2 is the number of grid points covering the rhombic bcc (110) substrate surface unit cell. A given E_{ij} corresponds to a configuration in which a given interfacial epilayer atom is centered above the grid point (x_{ij}, y_{ij}) surface unit cell, E_{ij} being the energy difference of stacks of atoms from the epilayer–substrate and the separated crystals. Analytical minimization of the sum of squares of the differences $E_{ij}-V^{(2)}(x_{ij},y_{ij})$ with respect to the coefficients V_{hk} yields the following relations for the optimized coefficients

$$V_{00}^{+}=\frac{1}{2K^2}\sum_{i,j}E_{ij},$$

$$V_{20}=\frac{1}{K^2}\sum_{i,j}E_{ij}\cos\left[4\pi\left(\frac{x_{ij}\sin\alpha-y_{ij}\cos\alpha}{2a\sin\alpha}\right)\right],$$

$$V_{02}=\frac{1}{K^2}\sum_{i,j}E_{ij}\cos\left[4\pi\left(\frac{x_{ij}\cos\alpha+y_{ij}\sin\alpha}{2a\cos\alpha}\right)\right],$$

$$V_{11}=\frac{1}{K^2}\sum_{i,j}E_{ij}\left\{\cos\left[2\pi\left(\frac{x_{ij}\sin2\alpha-y_{ij}\cos2\alpha}{d_a}\right)\right]+\cos\left(\frac{2\pi y_{ij}}{d_a}\right)\right\}. \quad (12a)$$

When we optimize for the series in Eq. (11a), V_{00}^{+} still has the same form, whereas the other optimized coefficients take the general form

$$V_{hk}=\frac{1}{K^2}\sum_{i,j}E_{ij}\left\{\cos\left[2\pi\left(\frac{hx'_{ij}}{a_x}+\frac{ky'_{ij}}{a_y}\right)\right]+\cos\left[2\pi\left(\frac{hx'_{ij}}{a_x}-\frac{ky'_{ij}}{a_y}\right)\right]\right\}. \quad (12b)$$

In Eq. (12a) we have used the notation V_{00}^{+} rather than V_{00} to indicate that the registry strain energy ϵ^{e} of the epilayer probe is part of the zero order term $2V_{00}^{+}$ calculated from the E_{ij}. Clearly the value of ϵ^{e} will be dominated by the interaction of epilayer atoms amongst themselves and with the average field emanating from the substrate and thus be nearly a constant. This constant will form part of the E_{ij} in Eqs. (12a) and (12b) and make no contribution to the summations involving the periodic factors. The values of the E_{ij} and hence V_{00}^{+} will also depend on the reference configuration, as indicated above.

The computations in Part 2 fixed this at two substrate atomic layers. If we want the average energy $\langle V\rangle \equiv 2V_{00}$ to be some measure of the epilayer–substrate bonding, the energy E_{ij} is calculated as the difference in energy of the bicrystal with equilibrated interlayer spacings and the two separated crystals — an equilibrated free standing epilayer and an equilibrated substrate with free surface. In this procedure the cohesive energies make no contribution.

The foregoing considerations on Fourier representations focus on the influence of substrate periodicity. The homogeneously deformed epilayer is likewise a source of periodic interaction for atoms of the substrate. The relevant equations for the epilayer may be written down by replacing (α, a, d_a) by (β, b, d_b). As the substrate is taken rigid, that is a and d_a fixed, the epilayer may deform, i.e. b and d_b may change as described by Eq. (4a)–(4c). Expressing the relations (11d) and V_{11} in (12a) or (12b) for the epilayer in terms of b and d_b renders them more convenient for handling epilayer periodicity. The EAM interaction potential in Eq. (10) is expressed in terms of electron densities and pair potentials. Since their periodicities are just those of the epilayer and substrate, their roles may also be described in terms of similar periodic functions.

3.3. Intralayer interaction: elastic approach

We assume that initially — at ML thickness — the epilayer is either strained into 2D registry with the substrate and relieves misfit strain by misfit vernier formation at DL thickness to a configuration which is otherwise strained — d_b into $\bar{d}_b$ — into row match ($\bar{d}_b = d_a$) with the substrate in KS orientation as discussed in relation to Eq. (2) with reference to Fig. 1, or that the original ML already grows in the latter configuration. The misfit strain $\bar{e}_y$, which is normal to the relevant atomic rows — the normal being taken as the y-direction — then has a magnitude almost equal to $|f_{\mathrm{KS}}|$ as may be inferred from Eqs. (2) and (4). We assume $|f_{\mathrm{KS}}|$ to be small. After exceeding a critical number $n = n_{\mathrm{c}}$ of MLs, the epilayer becomes unstable, some MS is relieved and the relevant atomic rows are no longer in registry. From the fact that the maximum strain is less than $|f_{\mathrm{KS}}|$ we may assume that the resulting disregistry is small enough so that (a) it may be satisfactorily modeled [12] in terms of a sequence of misfit dislocations and (b) the atomic interaction within the epilayer may be adequately described by the harmonic approximation, i.e. Hooke's law.

In the direction parallel to the matching atomic rows, the situation is significantly different. In this direction the disregistry is so large, i.e. near to 20% as argued above [9], that the accommodation of misfit may be approximated by a misfit vernier in which the oscillatory strains, characteristic of MDs, are absent [12]. The implication of this is that the corresponding external force — the net force exerted by the substrate on the epilayer in a direction parallel to the substrate — has negligible effect on the epilayer and may be taken to vanish ('floating layer'). The related deformation may thus be approximated by the Poisson strain.

The fact that the maximum strains are small enough for the intralayer atomic interaction to be handled in terms of the harmonic (elastic) approximation allows great simplification of the description of configurations with misfit dislocations after misfit strain relief, structures that would require massive numerical computation otherwise. Now we only need to apply EAM to compute the relevant elastic constants. The substrate is assumed to be 'thick' (its lateral dimensions fixed), i.e. it is taken 'rigid' except for interlayer relaxation.

The deformation of the epilayer may be dealt with as a boundary value problem in linear elasticity theory. The vacuum–epilayer interface is free of forces, i.e.

$$0 = \sigma_z = \tau_{xz} = \tau_{yz} \tag{13}$$

where σ_i and τ_{ij} are respectively linear and shear stresses. The forces emanating from the substrate are those responsible for deformation within the epilayer plane normal to the sequence of parallel atomic rows of relevance in Eq. (2). This implies that we may also take

$$\tau_{xy} = 0. \tag{14}$$

Eqs. (13) and (14) imply that the shear strains vanish, $e_{ij} = 0$.

The analytical problem is greatly simplified if we take Eqs. (13) and (14) to hold throughout the film thickness, i.e. that the strain gradient *normal* to the film plane vanishes. While this is justified for Eq. (14), it is 'exact' for Eq. (13) only if the epilayer is a ML for which the concept of a normal gradient is inappropriate. When the epilayer has grown to a multilayer and MDs are present, Eq. (13) does not allow fully for elastic relaxation. One may expect it still to yield acceptable results up to 3 ML, but after that to have only qualitative significance. For the determination of the growth mode, where the effect of substrate proximity is the main issue, acceptability up to 3 ML is normally adequate as this would cover more or less the substrate proximity range [7].

The appropriate [20,21] in-plane Hookean equations are of the form

$$\sigma_x = D_{11} e_x + D_{12} e_y, \quad \sigma_y = D_{22} e_y + D_{12} e_x;$$
$$D_{22} = D_{11}, \tag{15}$$

where e_x and e_y are the linear strains. The symmetric forms of these relations imply that the fcc {111} in-plane elastic isotropy of fcc crystals also applies to fcc {111} epilayers. The elastic constants D_{11} and D_{12} may be expressed in terms of cubic elastic constants c_{ij} [20,21]. Since, in the present problem, we have to allow for dependence of stiffness constants on epilayer thickness, such an exercise is not of real value except to highlight differences. Rather, it is necessary to calculate D_{11} and D_{12} directly for each thickness using EAM. For this purpose we note that the strain energy per interfacial epilayer atom, corresponding to the relations (15), may be written as

$$\epsilon = \tfrac{1}{2}\, \Omega D_{11}(e_x^2 + e_y^2 + 2\nu e_x e_y), \quad \nu = D_{12}/D_{11} \tag{16}$$

where Ω is the (epilayer) volume per interfacial epilayer atom.

The analytical calculations are further simplified by the fact, as argued above, that the deformation in the x-direction is determined by the Poisson phenomenon applicable here because of the vanishing of the external force in the x-direction [9]. If we assume that the MDs are long and straight and that the oscillatory strains and stresses generated by them are of short range, this creates a plane strain condition in which $e_x = \bar{e}_x$, where the average is determined by the resultant external force which vanishes. This condition is satisfied by taking the average $\bar{\sigma}_x = 0$. It accordingly follows from Eq. (15) that

$$e_x = -\nu \bar{e}_y. \tag{17}$$

3.4. EAM approach to elastic properties and equilibrium structure

For the present purpose the influence of a crystalline substrate on an epilayer can be classified into two categories: (i) the category that stems from the height and wavelength of the periodic undulations of the epilayer–substrate interaction could for example stabilize a coherent configuration and dominates the width of misfit dislocations when the epilayer is incoherent, or allows misfit dislocations to degenerate into a misfit vernier when the undulation amplitude is small enough and/or the misfit large enough — to be dealt with in Section 3.5 — and (ii) the category that effects the inherent properties, e.g. in-plane equilibrium structure, strain energy and stiffness of the epilayer. The overall equilibrium structure of a thin epilayer-thick substrate composite under quasi-equilibrium growth conditions involves equilibration (energy minimization) of: (a) interlayer spacings of the composite, (b) intralayer (in-plane) atomic spacings of the epilayer, (c) modes of misfit accommodation, and (d) modes of growth. Here we are specifically interested in the inherent elastic properties of a crystal, e.g. its stiffness constants, which are defined in terms of *homogeneous* deformations in a field free of lateral forces. We propose that the influence of the short wavelength periodic fields at the epilayer–substrate interface on the elastic properties of the epilayer may be defined in terms of homogeneous deformation and the misfit vernier mode of misfit accommodation within the 'smoothed' (averaged) fields of the composite. The 'fields' involve the epilayer within the periodic field of the substrate, and vice versa. A simplifying approximation, that facilitates the computational effort and is dealt with in Part 2, is that the energetic contribution of the substrate to the energy of lateral deformation is negligible. An important implication of this is that the substrate contribution can be ignored in computing the strain energy and equilibrium in-plane epilayer atomic spacings, except perhaps for Pt on Fe.

The total energy of the epilayer–substrate composite (bicrystal) under homogeneous (with misfit vernier mode of misfit accommodation) deformation $\bar{e}=(\bar{e}_x, \bar{e}_y)$ of an n ML thick epilayer may be expressed in the form [10]

$$E_n(\bar{e})=N^{E_\mathrm{P}}\langle E(\bar{e})\rangle^{E_\mathrm{P}}_{(n)}+N^\mathrm{S}(\bar{e})\langle E(\bar{e})\rangle^\mathrm{S}_{(n)} \tag{18a}$$

where N^{E_P} and $N^\mathrm{S}(\bar{e})\equiv N^\mathrm{S}[\bar{f}^{(n)}]$ have been defined in Eqs. (5)–(7) and $\langle E\rangle^{E_\mathrm{P}}_{(n)}$ [or $\langle E\rangle^\mathrm{S}_{(n)}$] is the average EAM energy of the epilayer (or substrate) per interfacial epilayer (or substrate) atom. According to Eq. (10) these are given by

$$\langle E\rangle^\mathrm{g}_{(n)}=\sum_{k=1}^{n}[F(\langle\rho_k\rangle)+\langle\phi_k\rangle]^\mathrm{g};\quad \mathrm{g}=\mathrm{Cu, Pd, Pt} \tag{18b}$$

$$\langle E\rangle^\mathrm{S}_{(n)}=\sum_{\alpha=a,b}[F(\langle\rho_\alpha\rangle)]^\mathrm{S} \tag{18c}$$

where the averages $\langle\rho\rangle$ and $\langle\phi\rangle$ are dealt with in Appendix C, the total pair bond energy $\langle\phi\rangle$ across the interface has been assigned to epilayer atoms and a, b, ... designate consecutive atomic layers of the substrate.

The strain energy per interfacial epilayer atom may accordingly be defined as

$$\epsilon_n(\bar{e})=\{E_n(\bar{e})-[E_n(\bar{e}_\mathrm{m})+E^\mathrm{S}_0\Delta N^\mathrm{S}]\}/N^{E_\mathrm{P}} \tag{19}$$

where E^S_0 is the EAM energy per surface atom of the free substrate 'surface' — 'surface' refers to the substrate atomic layers that are energetically influenced by the vacuum proximity and ΔN^S is the number of substrate surface atoms that become covered in the deformation ($\bar{e}$) starting at the equilibrium (energy minimized) value $\bar{e}=\bar{e}_\mathrm{m}$. Here the strain $\bar{e}$ is defined with respect to the bulk structure, so that $\bar{e}_\mathrm{m}$ is a measure of the extent to which the equilibrium in-plane spacings of the n-fold epilayer differ from that of the bulk crystal because of vacuum and substrate proximity. Note that energy minimization with respect to in-plane structure assumes already equilibrated interlayer spacings.

3.5. *Misfit accommodation in Kurdjumov–Sachs orientation*

The consequences for the growth mode of the possibility that at uniform ML coverage of the substrate the ML is fully (2D) coherent and that at DL coverage MS is relieved with a transition to the 1D KS misfit accommodation mode is dealt with in Appendices A and B — in Appendix A to analytically compare the relative importance of epilayer strain energy and epilayer–substrate interaction energy in effecting MS relief and in Appendix B by a discrete approach to assess the relative significance of substrate coverage change for MS relief and growth mode.

While the derivation of average energies for epilayers in which the misfit is accommodated by coherence or a misfit vernier, or a combination of the two, is fairly straightforward, the derivation for a configuration with MDs is more complicated though elegantly tractable by an analytical approach. Such an approach was first introduced by Frank and van der Merwe [22] and subsequently extended by van der Merwe [23]. A primary step is to determine the critical thickness n_c at which the growing epilayer with 1D coherence ($\bar{f}_y=0$) becomes thermodynamically unstable and above which the stable configuration is one with misfit dislocations at the interface. To apply the criterion for a transition to SK growth, which is the important issue, we also need to calculate the equilibrium energies before and after reaching the critical thickness. We thus also need to know the equilibrium configuration, including the misfit dislocation density ($\bar{f}_y$) and average energies. A simple analytical approximation, designed to meet the assumptions adopted here, has been used to calculate the desired quantities [9]. A major simplifying approximation is that the strain gradient normal to the interface plane — which would exist when misfit dislocations are present — is small enough to be ignored. While this is fair enough for a ML, it would introduce discrepancies of up to 10% or even more for epilayers with thickness $n \geq 3$ [24,25]. For the smaller thicknesses of interest here the error is believed not to be serious. The approach also does not account for free energy changes involved in substrate surface coverage changes generated during MS relief by MDs. We believe that the energetic discrepancies involved are small and that the model is accurate enough to predict reliable trends. Details of the energetics of coverage change are given in Appendix B.

The thermodynamic equilibrium of the configuration in which the deformation in the x-direction is accounted for by Poisson strain is determined in the model by the relation [9]

$$\frac{2E(\kappa)}{\pi\kappa L} - \frac{\pi\nu^2}{2L\kappa K(\kappa)} = (1-\nu^2)|f_y| \tag{20}$$

where $K(\kappa)$ and $E(\kappa)$ are complete elliptic integrals of the first and second kind, respectively, depending on the parameter κ, and L and ν are given in Eq. (23a). In the present case, the value of the parameter κ as obtained by solving Eq. (20) determines the dependence of the equilibrium misfit dislocation density $\bar{f}_y$ by the relation

$$\bar{f}_y = \pm \frac{\pi}{2L\kappa K(\kappa)}. \tag{21}$$

The critical thickness n_c, determined by the limit $\bar{f}_y \to 0$, is obtained when $\kappa = 1$ in Eqs. (20) and (21), to yield the equation

$$\frac{2}{\pi L} = (1-\nu^2)|f_y|, \quad n = n_c. \tag{22a}$$

This may also be rewritten in the form

$$\frac{\Omega D_{11}}{|V_{11}|} = \left[\frac{4d_b}{\pi d_a(1-\nu^2)f_y}\right]^2 \tag{22b}$$

using Eq. (23a). Note that in Eqs. (20)–(22) all the relevant quantities

$$L^2 = \frac{1}{4}\frac{\Omega D_{11}}{|V_{11}|}\left(\frac{d_a}{d_b}\right)^2, \quad \nu = \frac{\Omega D_{12}}{\Omega D_{11}}, \quad f_y = \frac{d_b}{d_a} - 1 \tag{23a}$$

except d_a are functions of n. Also of interest is the critical misfit f_y^c — criticality of a ML — which follows from Eq. (22a) as

$$|f_y^c| = \left[\frac{2}{\pi L(1-\nu^2)}\right]_{n=1}. \tag{23b}$$

The equilibrium values of V_{11}, ΩD_{11}, ΩD_{12} and d_b for $n = 1$, 2 and 3 are EAM calculated in Part 2.

3.6. Application to growth modes

To probe the role of misfit strain relief in the realization of growth modes we need to know, in principle, only the average total energies of the epilayer–substrate system for epilayers of three consecutive thicknesses. However, the question as to the individual contributions $\langle\epsilon\rangle_{MS}$ of homogeneous misfit strain and the energy $\langle V+\epsilon\rangle_{MD}$ assigned to misfit dislocations — originating from oscillatory strains and disregistry — to the total average energy per interfacial epilayer atom and hence to 3D growth has often been raised. The question can be dealt with by the present approach in terms of the calculated average contributions [9]

$$V_{\min} = 2V_{00} - |V_{11}| \tag{24a}$$

to the minimum average epilayer–substrate interaction energy of the 1D KS configuration, which is obtained at $\bar{f}_y = 0$ ($\kappa = 1$):

$$\langle\epsilon\rangle_{MS} = 2|V_{11}|L^2(1-\nu^2)(\bar{f}_y - f_y)^2 \tag{24b}$$

$$= 2|V_{11}|L^2(1-\nu^2)f_y^2; \quad \bar{f}_y = 0 \tag{24c}$$

$$\langle V+\epsilon\rangle_{MD} = 2|V_{11}|L^2\left[\frac{1}{L^2}\left(1-\frac{1}{\kappa^2}\right) + \frac{4E(\kappa)}{\pi\kappa L}|\bar{f}_y| - \bar{f}_y^2\right] \tag{24d}$$

$$= 0; \quad \bar{f}_y = 0. \tag{24e}$$

Note that all the quantities in Eq. (24a)–(24d) depend on n, i.e. account for proximity effects, that κ is the solution of Eq. (20) and that at and below the critical thickness $n=n_c$ ($\bar{f}_y=0$) the contribution assigned to the misfit dislocations vanishes. It is convenient to write the average energy, when $n<n_c$ in the form

$$E_n^{\text{reg.}}=2V_{00}-|V_{11}|+2|V_{11}|L^2(1-\nu^2)f_y^2 \equiv (V_{\min}+\langle\epsilon\rangle_{\text{MS}}^{\text{reg.}})^{(n)} \quad (25a)$$

and to denote the average when misfit dislocations are present ($n>n_c$) by

$$E_n^{\text{disreg.}}=(V_{\min}+\langle\epsilon\rangle_{\text{MS}}+\langle V+\epsilon\rangle_{\text{MD}})^{(n)}. \quad (25b)$$

Recall that 'registry' and 'disregistry' here only apply to the KS orientation in which 'reg.' designates 1D KS matching of a *set* of parallel close-packed atomic rows of the epilayer with a corresponding *set* in the substrate and 'disreg.' their non-matching involving MDs.

Computations of the critical thickness n_c using Eq. (22a) with parameters computed using EAM potentials predict that $n_c>3$ for the selected materials, and hence that MS relief by MDs, in these systems, does not fall within the validity regime of Eqs. (20)–(25). The conclusion that $n_c>3$ is confirmed by other approaches, e.g. the discrete approach of Appendix B. Growth modes may be expressed in terms of the formalism of Eqs. (24) and (25). It is more convenient though to do this according to the discrete approach — it has wider validity and generality, accounts for coverage change and is simplified by the fact that the optimum Fourier coefficients are already known at this stage.

It is important to remember that modes of misfit accommodation and growth are two distinct phenomena. The fact that they are governed by related physical quantities often generates some confusion. The criteria for two modes of misfit accommodation compare the energetics of the same system in two different modes generated by deformation with maintenance of contact between nearest neighbor epilayer atoms, whereas the criteria in Eq. (1) for growth modes compare two distinct configurations generated by transfer of material between two neighboring layers. The implications of the latter criterion have been dealt with in more detail with reference to Eq. (1b).

4. Discussion and conclusions

For fundamental and technological purposes thin films with perfection in crystallinity and thickness uniformity are ideally required. These ideals are best served by growing epitaxial films in modes of the pseudomorphic misfit accommodation and layer-by-layer growth. This study focuses on the properties — stiffness constants, misfit strain relief, growth modes, proximity, interfacial energy, etc. — of ultrathin (≤ 3 ML) films, making suitable choices of surface free energies and lattice parameters, one important objective being the significance of MS relief in the transition to SK growth, that is to non-uniform growth. In Part 1 we develop the necessary analytic descriptions of the relevant relations for quantification in Part 2, using EAM interaction potentials.

With a bcc (110) Fe substrate the epilayer materials Cu, Pt and Pd were believed to be promising materials for computation of the relevant properties, particularly with respect to misfit accommodation and growth modes. To facilitate the application of equilibrium principles and to assess the significance of coverage changes for misfit strain relief and growth modes the approach focuses on epilayers of finite extent on a thick substrate of large lateral extent.

Another important feature of the analytical approach is that stiffness constants are defined in terms of homogeneous deformation on a substrate for which the periodic variation of epilayer–substrate interaction potential is smoothed by averaging.

The results which follow directly from the analytic considerations are that (a) if proximity effects are neglected strain energy does not contribute to the growth mode discriminant defined in Eq. (1), whereas (b) misfit strain relief from the 2D coherent to a 1D KS mode of misfit accommodation is favored by large strain energy and large substrate surface free energy, but opposed by a strong epilayer–substrate interaction potential, a conclusion in agreement with expectation.

While, for the systems investigated, the effect of misfit strain relief by misfit dislocation formation on the growth mode discriminant and hence on SK growth could not be studied, it seems certain that systems in which misfit dislocation formation occurs at the ultrathin epilayer stage, where SK growth is relevant, should exist. Of particular interest in this case is the conclusion that bonding within the epilayer decreases with distance from the interface. It is conceivable that the bonding, as portrayed by the corrugation amplitude of interlayer interaction between the upper monolayer (or multilayer) and bicrystal substrate, decreases below a value at which misfit strain relief in the upper layer(s) becomes energetically favorable. Although it is true that SK growth by 'coherent islanding' is often observed and is apparently more probable, it may be interesting to exploit the possibility of misfit strain relief at an interface within the epilayer.

Appendix A: The transition from 2D coherence to 1D coherence in KS orientation

This transition is of great significance in the phenomena under consideration. It is therefore enlightening to analyze more fully the individual contributions of homogeneous strain energy (ϵ), epilayer atom–substrate interaction (V) and substrate surface free energy (Γ) to the driving energetics of the transitions, specifically their importance for the stability criteria for a ML as formulated in relation (B.4).

It follows from Eqs. (4)–(7) that, in the case of the 1D KS orientation ($\bar{d}_b = d_a$) the 1D KS MS is given by

$$\bar{e}_{\mathrm{KS}} = -\frac{d_a}{d_b}\left(\frac{d_b}{d_a} - 1\right) = \frac{r_{\mathrm{KS}}}{r} - 1. \tag{A.1}$$

Likewise we have for the 2D coherent configuration in NW orientation [12]

$$\bar{e}_i = \frac{r_i}{r} - 1; \quad i = x, y$$

$$r_x = \frac{\sin\alpha}{\sin\beta} \approx 0.934, \quad r_y = \frac{\cos\alpha}{\cos\beta} \approx 1.155. \tag{A.2}$$

If we substitute for $f_y \equiv f_{\mathrm{KS}}$ in Eq. (24c) and for $\bar{e}_i$ in Eq. (16), it follows, after some algebra, that

$$\begin{aligned}\epsilon_{2\mathrm{D}} - \epsilon_{1\mathrm{D}} = \frac{\Omega D_{11}}{2r^2}\{&(1+\nu)^2 r^2 \\ &- 2(1+\nu)[r_x + r_y - (1-\nu) r_{\mathrm{KS}}]r + (r_x + r_y)^2 \\ &- 2(1-\nu) r_x r_y - (1-\nu^2) r_{\mathrm{KS}}^2\}\end{aligned} \tag{A.3}$$

which is a quadratic expression in r. To determine whether the expression changes sign (vanishes) at some value of r, we calculate the relevant discriminant for the quadratic equation $ax^2 + bx + c = 0$, obtaining

$$b^2 - 4ac = 8(1+\nu)^2(1-\nu)(r_x - r_{\mathrm{KS}})(r_y - r_{\mathrm{KS}}).$$

This is negative and implies that the expression for $\epsilon_{2\mathrm{D}} - \epsilon_{1\mathrm{D}}$ never changes sign. Since the value of $\epsilon_{2\mathrm{D}} - \epsilon_{1\mathrm{D}}$ for $r = r_x$, i.e.

$$\begin{aligned}\epsilon_{2\mathrm{D}} - \epsilon_{1\mathrm{D}} &= \frac{\Omega D_{11}}{2r_x^2}(r_x - r_{\mathrm{KS}})^2\left[\frac{r_x - r_y}{r_x - r_{\mathrm{KS}}} - 1 + \nu^2\right] \\ &> \frac{\Omega D_{11}}{2r_x^2}(r_x - r_{\mathrm{KS}})^2 \nu^2 > 0\end{aligned} \tag{A.4}$$

is positive, it follows that it is everywhere positive, i.e. that the MS energy in the 2D coherent configuration always exceeds that in a 1D KS configuration and would suggest that 1D KS growth should form from the beginning. However, it is the total energy, which includes the opposing influence of the epilayer–substrate bonding, as expressed in terms of the optimum Fourier coefficients V_{hk}, that determines the stability of a given misfit accommodation mode, e.g. the 2D coherent configuration and would suggest that 1D KS growth should form from the beginning.

Also, for growth in KS orientation the relevant misfit $f_{\mathrm{KS}}(\equiv f_y) = d_b/d_a - 1$ must be small, i.e. $d_b/d_a \equiv r/r_{\mathrm{KS}} \approx 1$ [12]. It accordingly follows from Eq. (9) that

$$q(\bar{e}_{1\mathrm{D}}) - 1 \approx r - 1 \approx r_{\mathrm{KS}} - 1 \approx 0.089. \tag{A.5}$$

This is saying that a transition 2D→1D KS always occurs with increasing substrate coverage and implies that the term involving E_0^{S}, i.e. the surface free energy Γ of the substrate, also makes a positive contribution to Eq. (B.4) and a negative contribution to Eq. (B.2).

For growth on a bcc (110) substrate the direct contribution $2V_{20}+V_{11}+2V_{02}$ in Eq. (B.4), emanating from the epilayer–substrate bonding, is dominated by the negative term V_{11}, e.g. for a Ni ML on W(110) — a case of strong bonding across the interface — the EAM estimated values of $2V_{20}$, V_{11} and $2V_{02}$ to be respectively 0.082, −0.269 and −0.030 eV/Ni atom [10].

The message from this Appendix is that excess MS energy $\epsilon_{2D}-\epsilon_{1D}$ and large substrate surface free energy energetically favor the 1D KS configuration, whereas the 2D configuration is favored by strong interfacial bonding, as observed in the growth of Cu on W(110) [10]. Since strong interfacial bonding also correlates in EAM somewhat with large substrate surface free energy, the two features have a common source, but two opposing influences. The expression in Eq. (B.4) can also be used to support the suggestion that the instability of the 2D configuration increases with increasing epilayer thickness.

Appendix B: Discrete approach

B.1. Misfit accommodation

The '*discrete*' approach analyses misfit accommodation and growth modes from an atomic point of view rather than applying continuum theory. The application of energetic principles is furthermore facilitated by fixing the size of the physical system. We meaningfully select the size to be that of maximum coverage by the finite size epilayer, i.e. coverage in the 1D KS configuration. The total defect energy of the system in Eq. (18a) — accounting for substrate coverage — may accordingly be written as

$$E_n(\bar{e})=N^{E_P}\langle E(\bar{e})\rangle^{E_P}_{(n)}+N^{S}(\bar{e})\langle E(\bar{e})\rangle^{S}_{(n)}+\Delta N^{S}(\bar{e})E^{S}_{0}\delta \tag{B.1}$$

where $\delta=0$, 1 for $\bar{e}=\bar{e}_{1D}$, $\bar{e}_{2D}$, respectively, $\langle E(\bar{e})\rangle_{(n)}$ is the average energy per interfacial atom in the presence of a n ML thick epilayer, the numbers N^{E_P}, N^S and ΔN^S are defined in Section 2 and the surface free energy per atom of the substrate Γ and E^S_0 of Eq. (1a) are related by $\Gamma=E^S_0-m\epsilon^S_{\mathrm{coh}}$, m being the number of substrate layers that energetically experience the presence of the interface. Note that by definition E^S_0 is negative and that it accounts for Γ in the relations below.

The stability of an n ML thick epilayer in the 2D≡(reg.-y, reg.-x) configuration compared with the 1D KS configuration is determined by excess energy per interfacial epilayer atom:

$$\begin{aligned}\Delta E^{(n)}_{2D,1D}=&[\langle E(\bar{e}_{2D})\rangle^{E_P}+q(\bar{e}_{2D})\langle E(\bar{e}_{2D})\rangle^{S}]^{(n)}\\&-[\langle E(\bar{e}_{1D})\rangle^{E_P}+q(\bar{e}_{1D})\langle E(\bar{e}_{1D})\rangle^{S}]^{(n)}\\&+[q(\bar{e}_{1D})-q(\bar{e}_{2D})]^{(n)}E^{S}_{0}\end{aligned} \tag{B.2}$$

where q is defined in Eq. (8). If the excess is positive the 2D configuration is unstable.

A notable effect, which is a consequence of accounting for the substrate coverage, is that the quantity $q(\bar{e}_{1D})-q(\bar{e}_{2D})$ introduces some asymmetry depending on the sign of the misfit. This conclusion also applies to the relations below. Furthermore, in the classical theory of epitaxy the change of substrate coverage, involved in MS relief, is ignored. A rough estimate shows that the factor $q(\bar{e}_{1D})-q(\bar{e}_{2D})\approx 0.1$, which means that the discrepancy may be significant depending on the relative values of the defect energies related to DLs, MLs and free substrate surfaces.

The quantities in the first and second square bracket of Eq. (B.2) can be expressed in terms of the Fourier coefficients V_{hk} and MS energies ϵ to yield, after some simplification, the result

$$\begin{aligned}\Delta E^{(n)}_{2D,1D}=\{&2V_{20}+V_{11}+2V_{02}+\epsilon_{2D}-\epsilon_{1D}\\&+[q(\bar{e}_{1D})-1]^{(n)}E^{S}_{0}\}\end{aligned} \tag{B.3}$$

where $\epsilon_{2D}\equiv\epsilon^{e}$ and ϵ_{1D} is the MS energy in the 1D KS configuration, i.e. Eq. (24c). Recall that the potential energy undulations V_{hk} for $h+k\geq 2$ are independent of the energy reference, whereas the constant term is not.

The formulation of misfit accommodation stability and growth mode criteria in terms of optimum Fourier coefficients V_{hk} and MS energy ϵ is convenient if the V_{hk} and ϵ have been quantified already. Alternatively, it could be useful in checking the degree of agreement between the two approaches.

B.2. Growth modes

We demonstrate the application to growth mode realization in terms of two simple cases, an epilayer with (i) incomplete ML and DL regions, respectively in 2D and 1D KS misfit accommodation modes, and (ii) a complete ML and incomplete DL and TL regions each in either of 2D and 1D KS modes. To derive the growth mode discriminants we imagine the transfer of n^{E_P} atoms from the upper to the next lower ML. In case (i) this implies, for example, the trading of $n^\mathrm{S}_\mathrm{DL}(\bar{e}_\mathrm{1D})$ covered substrate surface atoms from the DL portion for $2n^\mathrm{S}_\mathrm{ML}(\bar{e}_\mathrm{2D})$ covered substrate surface atoms from the ML portion, i.e. there have been $2n^\mathrm{S}_\mathrm{ML}(\bar{e}_\mathrm{2D})-n^\mathrm{S}_\mathrm{DL}(\bar{e}_\mathrm{1D})$ more uncovered substrate surface atoms in the initial than in the final configuration. Furthermore, the ratios $n^\mathrm{S}/n^{E_\mathrm{P}}$ take the same form as $N^\mathrm{S}/N^{E_\mathrm{P}}$ in Eqs. (8) and (9) — hence

$$[2n^\mathrm{S}_\mathrm{ML}(\bar{e}_\mathrm{2D})-n^\mathrm{S}_\mathrm{DL}(\bar{e}_\mathrm{1D})]/n^{E_\mathrm{P}}=2-q_\mathrm{DL}(\bar{e}_\mathrm{1D});$$

$$n^\mathrm{S}(\bar{e}_\mathrm{2D})=n^{E_\mathrm{P}}.$$

The growth mode discriminant for case (i), when expressed in terms of Fourier coefficients and average energies per epilayer atom, becomes

$$\begin{aligned}\Delta E^\mathrm{1D,2D}_{21}=&2[2V_{00}+2V_{20}+2V_{11}+2V_{02}+\epsilon_\mathrm{2D}]^\mathrm{2D}_\mathrm{ML}\\&-[2V_{00}+V_{11}+\epsilon_\mathrm{1D}]^\mathrm{1D}_\mathrm{DL}-[2-q_\mathrm{DL}(\bar{e}_\mathrm{1D})]E^\mathrm{S}_0\end{aligned} \tag{B.4}$$

Following the arguments that yield the relation (B.4), the growth mode discriminant for the growth of the *n*th ML — neglecting coverage change — is given in Eq. (1b). Eq. (1b) may be rewritten in terms of defect energies — for the growth of the first ML as:

$$\begin{aligned}\Delta E_{2,1}=&2[E_\mathrm{ML}-\epsilon^{E_\mathrm{P}}_\mathrm{coh}-m\epsilon^\mathrm{S}_\mathrm{coh}]-[E_\mathrm{DL}-2\epsilon^{E_\mathrm{P}}_\mathrm{coh}\\&-m\epsilon^\mathrm{S}_\mathrm{coh}]-[E^\mathrm{S}-m\epsilon^\mathrm{S}_\mathrm{coh}]\end{aligned} \tag{B.5}$$

where ϵ_coh designates cohesive energy per ML per unit area. If we assume that the concepts of surface and interfacial energies are valid for ML and DL coverages, Eq. (B.5) becomes

$$\Delta E_{2,1}\equiv\Delta\gamma=2(\gamma_0+\gamma_\mathrm{i})-(\gamma_0-\gamma_\mathrm{i})-\gamma_\mathrm{s}=\gamma_0+\gamma_\mathrm{i}-\gamma_\mathrm{s} \tag{B.6}$$

which is the growth mode discriminant of Bauer [1] in Eq. (1a).

Appendix C: Averages

For misfit accommodation by a misfit vernier all periodic terms vanish on averaging. In a representation such as Eq. (11), the average of the term in V_{11} would vanish in a 2D vernier, whereas it would contribute an amount V_{11} to the average before misfit strain relief of the 1D KS configuration. We may accordingly write

$$\langle V\rangle=2V_{00}+V_{11}\delta \tag{C.1}$$

for the average of the epilayer–substrate interaction, where $\delta=1$ and 0 before ($\bar{f}_y=0$) and after ($\bar{f}_y\neq0$) misfit strain relief, respectively. Note that this discontinuity applies when the mode of misfit accommodation changes from a misfit vernier to MDs.

In calculating energies of homogeneous strain we need average embedding and pair potential energies for a misfit vernier mode of misfit accommodation. It has previously [10] been shown that, for a completely non-matching epilayer in misfit vernier mode on a (110) bcc substrate, the average embedding energy for atoms in layer k of the epilayer may be expressed fairly accurately in terms of the average electron density $\langle\rho_k\rangle$ as

$$\langle F(\rho_k)\rangle\approx F(\langle\rho_k\rangle);\quad \langle\rho_k\rangle=\rho_k+2\rho^{k\text{–}\mathrm{S}}_{00} \tag{C.2}$$

where $\rho_k\equiv\rho^{E_\mathrm{P}}_k$ is the electron density at an epilayer atom in layer k due to the remaining epilayer atoms and $2\rho^{k\text{–}\mathrm{S}}_{00}$ the average there due to the periodic field of the (110) bcc substrate (S). The average pair potential energy that may be assigned to an atom in layer k is given by

$$\langle\phi_k\rangle=\tfrac{1}{2}\,\phi_k+2\phi^{k\text{–}\mathrm{S}}_{00}p \tag{C.3}$$

where ϕ_k is the pair bond energy of an epilayer atom in layer k with respect to all other epilayer atoms and $2\phi^{k\text{–}\mathrm{S}}_{00}$ the average pair bond energy of an atom in layer k with the substrate atoms. In calculating the homogeneous strain energy in the epilayer it is convenient to assign the full bond energy ($p=1$) to the epilayer atom as in Eq. (18b). An atomic layer of the substrate may be similarly described, except that there is no contribution $\phi_{00}^{\alpha-E_\mathrm{P}}$ from the epilayer in Eq. (18c) to the average pair potential energy of the substrate — the total pair potential energy having been assigned to the epilayer atom.

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