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Composition modulation and nanophase separation in a binary epilayer

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Abstract

When a thin binary layer grows epitaxially on an elemental substrate, the composition often modulates in the plane of the layer. The layer may even demix when the bulk of the same composition is miscible. Sometimes the layer separates into two phases, forming periodic stripes or other regular patterns. The size of the separated phases may be in the range 1–100 nm, and stable against coarsening on annealing. This paper develops a thermodynamic framework to study these remarkable phenomena. For an epilayer less than a few monolayers thick, the excess energy cannot be attributed to individual sources of superficial misfit. Instead, we lump the epilayer and adjacent monolayers of the substrate into a single superficial object, and specify the excess surface energy for the object. The variation of the surface energy density with the variation of the strain defines surface stress. When the composition modulates in the epilayer, the surface stress is nonuniform, deforms the substrate, and reduces the total energy. Consequently, the composition-dependent surface stress tends to refine phases, resisting coarsening. In a stability analysis, we perturb a uniform concentration field into a sinusoidal field with a small amplitude and an arbitrary wavelength. The entropy of mixing stabilizes the uniform layer for long wavelengths. To stabilize the uniform layer for short wavelengths, we assume that the surface energy density also depends on concentration-gradient. A stability condition shows the combined elastic, entropic, and gradient effects. We also outline a dynamical system, which can be used to study pattern emergence and evolution during annealing. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Modern electronic and photonic devices are solid structures of small feature sizes. During fabrication, processes like diffusion relocate atoms, and the structures evolve over time. Such a structural change is a nuisance when, for example, a film breaks into droplets, or an unexpected phase appears. Yet the changes themselves can be exploited to fabricate devices (Pearsall and Stringfellow, 1997; Zunger, 1998). In either case, as feature sizes decrease, insight into forces operating in small dimensions becomes indispensable. Self-assembled nanostructures pose fascinating mechanics problems; see reviews by Freund (1999), Gao and Nix (1999), Peralta et al. (1998), and Suo (1999).

This paper studies demixing behaviors in binary epitaxial layers. For example, when less than half a monolayer quantity of Ag is deposited on a Pt substrate, at an elevated temperature, diffusion of Ag is rapid within the topmost layer, but negligible in the bulk of the Pt substrate (Röder et al., 1993). Consequently, Ag atoms incorporate into the topmost layer and, together with Pt atoms, form a substitutional alloy. Within this layer, Ag atoms gather into nanometer clusters in the Pt matrix. Ibach (1997) reviewed several experimental systems that exhibit phase separation within superficial layers. In some systems the two phases may self-assemble into periodic stripes or other regular patterns (e.g., Kern et al., 1991; Pohl, et al., 1999). A key difference between the separated phases in bulk and on surface is that, upon annealing, the former undergo the Ostwald ripening, but the latter may equilibrate at a certain size scale, often in the range 1 to 100 nm. Multi-component semiconductor epitaxial films are used to tailor electronic energy band gap and to match lattice constant with the substrate. Composition modulation occurs in many such systems, as reviewed by Guyer and Voorhees (1998). In particular, it occurs in $\text{Si}_{1-x}\text{Ge}_x$ films grown on Si substrates, even though bulk Si and Ge are miscible at the temperature of film growth.

Often the epilayer thickness and composition both modulate. Theories for the coupled modulation have been advanced (Guyer and Voorhees, 1998; Glas, 1997). Nonetheless the two types of modulation need not coexist. Many epilayers are known to be flat when they are thin (Suo and Zhang, 1998). To focus on the novel aspects of this paper, we take the epilayer to be flat: its composition can modulate, but its thickness does not. By a flat epilayer we do not exclude atomic scale features on a surface, such as vacancies, adatoms, and steps — so long as the composition modulates over a length scale larger than the atomic dimension. In fact, these atomic surface features are needed to mediate diffusion. Steps may even be part of the phase structure, e.g., as phase boundaries.

Viewing a superficial alloy as a two-dimensional analogue of a bulk alloy, one

may use the energy-composition curve to understand the epilayer stability. If the curve is convex down, the alloy is miscible, and the layer is uniform. If the curve is convex up, the alloy is immiscible, and the layer separates into two phases. This view is too simplistic, however. It often gives wrong predictions. Consider the following two differences between a bulk and an epilayer.

First, when an epilayer is a few monolayers thick, it has a different energy-composition curve from the bulk, as affected by several sources of misfit: atomic sizes, chemical bonds, and the free space. Many authors separate the total energy into the energy of the epilayer surface, of the epilayer–substrate interface, of the epilayer bulk, and of the elastic deformation. The separation is meaningful when the epilayer is thick enough to be regarded as a bulk, but meaningless when the epilayer is less than a few monolayers thick. For example, the measured residual stress in a few monolayers of Ag on a Pt substrate is several times that calculated on the basis of lattice constant misfit (Grossmann et al., 1996; also see a correction in Ibach, 1997, Fig. 33). Even atoms at the surface of a pure crystal are subject to residual stress (see below).

Second, the superficial alloy is not strictly two dimensional. In the example of Ag on Pt, the topmost layer is an epitaxial extension of the Pt substrate. That is, the strong interatomic bonds require that Ag atoms occupy the sites that would be occupied by Pt atoms in a pure substrate. The epilayer and the substrate interact. The interaction, in its turn, may affect the distribution of Ag atoms in the epilayer. Various sources of superficial misfit cause a residual stress field. When Ag atoms are uniformly distributed in the epilayer, the residual stress field is localized within the superficial object, and the substrate bulk is stress-free. When the composition modulates over some large length scale, an elastic field arises and extends into the substrate to a depth of comparable length scale. The deformation changes the total energy. Consequently, the elastic substrate participates in the process of total energy minimization.

To paraphrase these in a continuum language requires the concepts of surface energy and surface stress. To fix the idea, first consider an elemental crystal. The atoms at the surface of the crystal have a different bonding environment from those in the bulk. Consequently, the energy per atom at the surface differs from that in the bulk, giving rise to the surface energy. The bonding difference also causes a residual stress field in the first few monolayers at the surface. More precisely, the surface energy density is the excess energy per unit surface area. The surface stress is the variation of the surface energy density with the variation of the strain parallel to the surface, keeping the number of lattice sites constant on the surface.

For an epilayer less than a few monolayers thick, it is impossible to attribute the energy to individual kinds of misfit. Instead, we will lump the whole epilayer, plus the adjacent monolayers of the substrate, into a single superficial object, and specify the energy for this object. In a way similar to elemental crystal surface, we can define surface energy and surface stress for an epilayer. As a result, our model differs from those of Guyer and Voorhees (1998) and Glas (1987, 1997), who

treated the case where the epilayer can be considered as a bulk. We will show that the composition-dependent surface stress reduces the total energy.

Conceptually, phase separation in a binary epilayer relates to surface domains on an elemental crystal. For example, a reconstructed silicon (100) surface has two variants of the same configuration, except for an in-plane 90° rotation. The two variants form domains much larger than the atomic dimension. Subject a silicon wafer to a bending moment, and the domains of one variant enlarge at the expense of the other (Men et al., 1988). The model of Alerhand et al. (1988) highlights two competing effects: surface stress anisotropy and domain wall energy. For each variant, the surface stresses are different in the two orthogonal directions. The difference gives rise to a line force at each domain wall. The elastic deformation of the crystal allows the force to reduce the total energy. Consequently, the surface stress anisotropy tends to refine domains: the smaller the domains, the lower the energy. Yet as the domain size decreases, the total length of the domain wall increases, so does the total domain wall energy. Consequently, the domain wall energy causes the domains to coarsen. As a result of this competition, the domains reach an equilibrium size. The effect of the bending moment is also readily understood in this model. An analogous model has been independently developed for epitaxial ferroelastic films (Pompe et al., 1993). (In fact, the phenomenon on silicon surface may be called superficial ferroelasticity. The phenomenon is surprising because bulk silicon is not ferroelastic. By analogy, a non-ferroelectric crystal may break symmetry on its surface, and exhibit superficial ferroelectricity.)

Our present paper differs from those of Alerhand et al. (1998) and Pompe et al. (1993) in several ways. We will consider a binary epilayer, so that the surface stress nonuniformity originates from composition modulation, rather than structure variants. More importantly, in a binary epilayer the entropy of mixing and the enthalpy of mixing and epitaxy play roles, along with the surface stresses and the phase boundaries. On an elemental crystal surface the surface stress anisotropy should always cause domains in equilibrium. In a binary epilayer, however, the entropy of mixing may be potent enough to stabilize a uniform epilayer. We are interested in the emergence and evolution of surface patterns, as well as their equilibrium size. Consequently, the model of a sharply defined phase boundary is unsuitable. To prevent concentration fluctuation in small length scales, we use a concentration-gradient term to represent the phase boundary energy, analogous to that of Cahn and Hilliard (1958) for bulk alloys.

At the root of the unusual demixing behaviors in a binary epilayer is that nonuniform surface stress tends to refine phases, resisting coarsening driven by gradient energy. The concept of surface stress in solid state was introduced by Gibbs (1878, p. 315). Cammarata (1994), Cammarata and Sieradzki (1994), and Ibach (1997) have reviewed many of its experimental consequences. The surface stress has been incorporated into continuum elasticity theory by including strain-dependent surface energy in addition to bulk elastic energy (e.g., Willis and Bullough, 1969; Gurtin and Murdoch, 1975; Rice and Chuang, 1981; Wu, 1996; Freund, 1998). The elasticity theory has so far been restricted to elemental solids.

This paper extends the theory to a binary epilayer on an elemental substrate. The surface energy density is now a function of strain, concentration, and concentration-gradient. The total energy can vary by two independent means: elastic distortion and species redistribution. An isothermal process is considered; the energy to be minimized is either the Helmholtz free energy in the absence of an external load, or the Gibbs free energy if a constant load is applied. With the specific application in mind, we present the theory within the framework of small strain elasticity.

The plan of the paper is as follows. We first specify the excess energy of the system (an epilayer on a substrate) relative to the unstrained infinite crystals of elemental constituents. The surface energy is defined by this excess energy minus bulk elastic energy. We prescribe the surface energy density as an explicit function of the strain, the concentration, and the concentration-gradient. We then consider the total energy variation with the strain and the composition variation, leading to the mechanical and the chemical equilibrium condition. A dynamical system is set up within the framework of linear nonequilibrium thermodynamics. We examine the stability of a uniform epilayer against small perturbations in the concentration field, and examine the combined effects of mixing, misfitting, straining, and gradient.

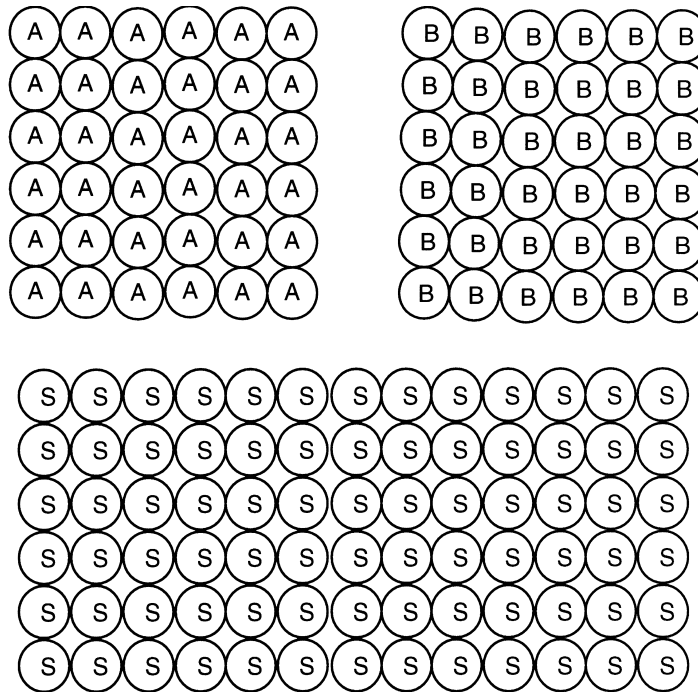


Fig. 1. The reference state: three isolated, unstrained, infinite crystals of elements A, B, and S.

2. Excess energy: mixing, misfitting, and straining

Fig. 1 illustrates isolated crystals of three elements, ‘A’, ‘B’ and ‘S’. Each crystal is infinite, pure, and unstrained. Denote the energy per atom in each crystal by μ_A , μ_B and μ_S , respectively. In this elemental state, N_A atoms of A, N_B of B, and N_S of S have the combined energy

$$\mu_A N_A + \mu_B N_B + \mu_S N_S. \quad (1)$$

This state will be used as the reference to define the excess energy of a system assembled from the three types of atoms.

Fig. 2 illustrates a system assembled with N_A atoms of A, N_B of B, and N_S of S. A layer of A–B mixture lies on a flat substrate of S. One element of the layer can be the same as that of the substrate, as in the example of Ag on Pt. Alternatively, the two elements of the layer can be both different from that of the substrate. The layer is an epitaxial extension of the substrate: A and B atoms occupy the sites that would be occupied by S atoms in a pure substrate. The epilayer is a substitutional alloy; the two species can relocate by diffusion. The relocation, however, is restricted within the layer, so that the substrate is pure, and the epilayer flat. In practice, for atoms to diffuse in the epilayer but not into the substrate, the epilayer should either be limited to very few monolayers, or have a much larger diffusivity than the substrate, or grow slowly to allow the atoms to diffuse on the surface before being buried. To be definite, in this paper we will consider a very thin epilayer with a fixed thickness. We are interested in the concentration distribution in the plane of the epilayer, but not in the thickness of the epilayer. Consequently, the concentration of the epilayer, C , is specified by the number of A atoms per unit area. A coordinate system is attached, x_1 and x_2

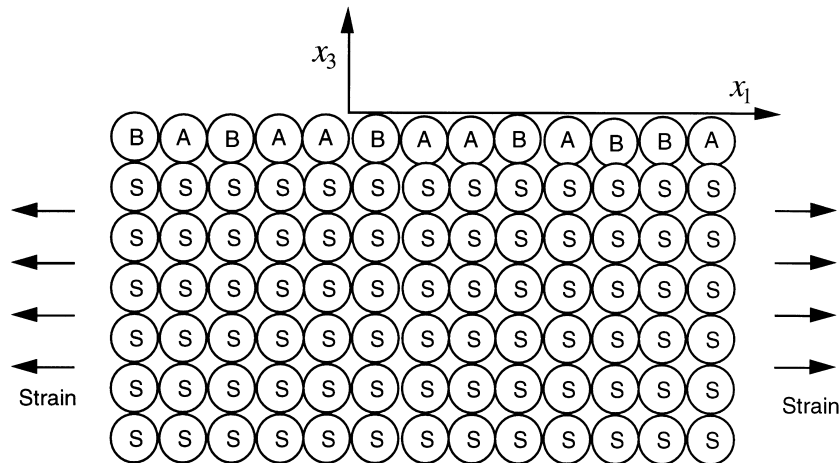


Fig. 2. Cross-sectional view of a binary epilayer on an elemental substrate subject to a strain.

lying in the plane of the epilayer, and x_3 being normal to the plane. For a nonuniform epilayer, the concentration is a function of position, $C(x_1, x_2)$.

The system in Fig. 2 differs from the reference state in Fig. 1 in three ways. First, atoms A and B are now mixed in the epilayer. For the time being, the concentration in the epilayer is constrained to be uniform. The mixing increases entropy and by itself reduces free energy. Second, the system relaxes to an equilibrium state (subject to the constraint of concentration uniformity) by accommodating the misfits among the three kinds of atoms and the free space. The misfits alter electronic states, changing the energy of the system. The effect is short-ranging in that atoms in the substrate, a few monolayers beneath the epilayer, have the same energy as those in an infinite elemental crystal of S subject to the same macroscopic strain field. We lump the epilayer, together with those adjacent monolayers of the substrate affected by the atomic misfit, into a single superficial object. Third, the system may be subject to a state of elastic strain, displacing atoms by small amount, but preserving the lattice structure. This is a long-range effect throughout the bulk of the system.

Let G be the excess of the energy of the actual system in Fig. 2 (including all the effects of mixing, misfitting, and straining) over that of the elemental crystals given by (1). That is, G is the work done to assemble atoms from the elemental state in Fig. 1 into the system of the epilayer on the substrate in Fig. 2. In principle, G can be calculated by using an atomistic model. The actual value of the reference energy (1) does not affect the process of relocating atoms A and B, keeping the number of each species constant.

For an epilayer on a semi-infinite substrate, the strain vanishes except in the superficial object, in which the excess energy G is confined. Let Γ be the excess energy G divided by the surface area A . Thus,

$$G = \Gamma A. \quad (2)$$

We will still call Γ the surface energy density, for want of a better name. Imagine a cylindrical surface of a unit cross-sectional area, with its axis normal to the epilayer. As defined, Γ is the work done to assemble atoms from the reference state in Fig. 1 into what is inside the imaginary cylindrical surface. Evidently, Γ depends on the composition and the thickness of the epilayer. The thickness dependence affects the shape stability of the epilayer (Chiu and Gao, 1995; Suo and Zhang, 1998). This paper treats a flat epilayer of a fixed thickness, and does not consider the thickness dependence explicitly.

Next consider the effect of strain. We will only allow elastic deformation — that is, the layer remains epitaxial to the substrate, with no defects such as misfit dislocations. Subject the system to an elastic strain parallel to the surface, and keep the number of atomic sites constant at the surface. The strain perturbs the electronic state everywhere, in the superficial object, as well as in the bulk. The state of an unstrained infinite elemental crystal S in Fig. 1 is well defined, relative to which we define the strain in the substrate bulk in Fig. 2. The strain state of the atoms in the superficial object is difficult to define. However, so long as the

epilayer remains epitaxial, the strain state in the superficial object is not an independent thermodynamic variable; we can use the strain in the substrate bulk, approaching the surface, to describe the thermodynamic state of the superficial object. In the spirit of Gibbs (1878, pp. 219–224), we will separate the surface and the bulk energy as follows.

When the surface and the bulk properties are isotropic, the residual stress in the superficial object induces a uniform strain field in the substrate of a certain shape, such as a sphere, an infinitely long cylinder, and an infinite sheet, provided the entire substrate surface is covered by the epilayer. Consider such a uniform state for the time being. We find the strain in the substrate bulk, and compute the elastic energy per unit volume, W , as in the elasticity theory. Imagine a surface enclosing a portion of the crystal S in the reference state, consisting of $N_S + N_A + N_B$ number of S atoms. The portion has the general shape of the actual system in Fig. 2. In the reference state, let V be the volume of the crystal inside the imaginary surface, and A be the area of surface that would be replaced by the epilayer. Define the surface energy ΓA as the excess energy of the actual system, G , minus the elastic energy that the system could have if the bulk elastic energy density and the matter were uniform all the way to the surface, WV . Thus,

$$G = WV + \Gamma A. \quad (3)$$

This separation of the bulk and the surface energy is fundamentally arbitrary. It is useful because, once the long-range strain field is subtracted, the superficial effect is short-ranged. Following Cahn (1980) and others, we take area A to be that of the undeformed substrate — that is, the area in the reference state. This choice makes it simpler to calculate energy variation because on straining, only Γ varies, but A remains the same. Some authors have used the deformed area instead, leading to a more complicated expression for surface stress.

In the above, the strain field in the bulk is generated entirely by the superficial misfit. If there is an external force, (3) should include a term of force times displacement, and G becomes the Gibbs free energy. In the linear elastic theory, the strain field caused by the superficial misfit and that by the external force can be superimposed. To focus on our main interest, here we assume that no external force is applied.

3. Nonuniform system, energy variation, and equilibrium condition

In the above section, to define Γ , we have taken the position that the total excess energy G and the bulk elastic energy WV are known, for example, from an atomistic calculation. In this section, we will take a different position. We will prescribe phenomenological expressions for Γ and W , and then use them to compute the total excess energy of the system G .

We have so far considered a uniform epilayer and a uniform strain field. To define the energy densities W and Γ , we have assumed that the system has reached

equilibrium subject to the constraint of uniformity. As stated above, such uniformity is possible only for substrates of special shapes. Furthermore, as will be evident later, even the state of a uniform epilayer on a strain-free semi-infinite substrate may not be a stable equilibrium state. Once the constraint of uniformity is removed, the system may further reduce energy by means of atomic diffusion and elastic deformation. The relaxed system has nonuniform concentration and strain fields.

We adopt the usual local equilibrium assumption. Within the framework of the continuum theory, even though the overall system is not in equilibrium, the energy densities W and Γ are defined for differential volume and area elements of the system, dV and dA . When the field is nonuniform, we still denote by G the excess of the energy of the system over the value (1) of the reference state. The excess energy is the sum of two integrals:

$$G = \int W dV + \int \Gamma dA. \quad (4)$$

There is a generalization of (3) to a nonuniform system. The integrals extend over the volume and area in the reference state of the S crystal. Eq. (4) is the foundation on which one can extend the classical elasticity theory, and is formally the same as that in the work of Freund (1998) and others cited in the Introduction. In this paper, however, the total energy can vary by means of both elastic deformation and species redistribution. We will prescribe the general forms of the energy densities, Γ and W , and derive the equilibrium conditions from the variation of the total energy.

Let u_i be the displacements of material particles relative to the unstrained substrate, and ϵ_{ij} be the strains. A Latin letter in a subscript runs from 1 to 3. The strains relate to the displacements in the usual way:

$$\epsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}). \quad (5)$$

A comma in a subscript denotes a partial differentiation with respect to a spatial coordinate. The displacement field is defined in the entire reference volume,

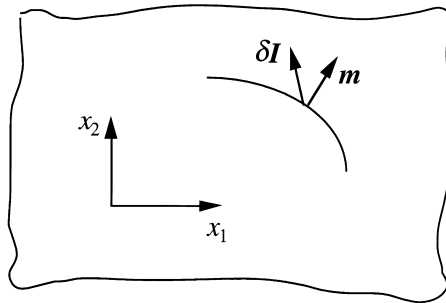


Fig. 3. The plane of the epilayer.

disregarding the dissimilarity between the bulk and the superficial object. The surface strains relate to the gradients of the surface displacements u_1 and u_2 in the same way:

$$\epsilon_{\alpha\beta} = \frac{1}{2}(u_{\alpha, \beta} + u_{\beta, \alpha}). \quad (6)$$

A Greek letter in a subscript runs from 1 to 2.

The epilayer is a binary substitutional alloy. Fig. 3 shows a plane view of the layer, with an imaginary curve in it. When some number of A atoms cross the curve, to maintain a flat epilayer, an equal number of B atoms must cross the curve in the opposite direction. Denote the unit vector normal to the curve by \mathbf{m} . Define a vector field \mathbf{I} in the surface (called mass displacement), such that $I_\alpha m_\alpha$ is the number of A atoms across a unit length of the curve. The quantity \mathbf{I} parallels a more familiar quantity, the mass flux \mathbf{J} , in the same way as the displacement parallels the velocity. The conservation of the occupied sites requires that the variation in the concentration relate to the variation in the mass displacement as

$$\delta C = -\delta I_{\alpha, \alpha} \quad (7)$$

with the summation convention implied.

The two vector fields, \mathbf{u} and \mathbf{I} , are basic kinematic variables; they vary independently, subject to no constraint. The compatible variation of the strains and of the concentration follow (5)–(7).

As usual, the strain energy density is prescribed as a function of strains, $W(\epsilon_{ij})$. When the strains vary from ϵ_{ij} to $\epsilon_{ij} + \delta\epsilon_{ij}$, the elastic energy density also varies. Write

$$\delta W = \sigma_{ij} \delta\epsilon_{ij}. \quad (8)$$

The partial differential coefficients σ_{ij} are the stresses. When the energy density is quadratic in the strains, the stresses are linear in the strains. This specialization will be made in the next section, but is unnecessary at this point.

The surface energy density Γ depends on the composition C and the strains parallel to the surface, $\epsilon_{\alpha\beta}$. As mentioned in the Introduction, we also need the composition gradients, $C_{,\alpha}$, as a variable to describe the thermodynamic state. Thus, the surface energy density is prescribed as a function $\Gamma(C, C_{,\alpha}, \epsilon_{\alpha\beta})$. The function is arbitrary at this point; an explicit form will be given in the next section. When the independent variables change, the surface energy density changes as

$$\delta\Gamma = \chi\delta C + \xi_\alpha\delta C_{,\alpha} + f_{\alpha\beta}\delta\epsilon_{\alpha\beta}. \quad (9)$$

The partial differential coefficients $f_{\alpha\beta}$ are the surface stresses; they form a tensor, and have the unit of line tension (force per unit length). In general, the surface stress is a function of concentration, concentration-gradient, and strain. No suitable names exist for the other two types of partial differential coefficients, χ and ξ_α , but their meanings are clear from the above expression.

As the two species A and B relocate in the epilayer, the total energy changes. Because no atoms are added to or removed from the system, the reference area and the reference volume remain the same as the two species redistribute. The total energy variation is due entirely to the variations in the energy densities:

$$\delta G = \int \delta W \, dV + \int \delta \Gamma \, dA. \quad (10)$$

The first integral is the same as in the classical elasticity theory. Using (5) and (8), one obtains that

$$\int \delta W \, dV = \int \sigma_{ij} \delta u_{i,j} \, dV = \int [(\sigma_{ij} \delta u_i)_{,j} - \sigma_{ij,j} \delta u_i] \, dV.$$

The divergence theorem transforms the first term in the bracket into a surface integral, giving

$$\int \delta W \, dV = \int \sigma_{ij} n_j \delta u_i \, dA - \int \sigma_{ij,j} \delta u_i \, dV. \quad (11)$$

The vector \mathbf{n} is the local normal of the surface. The surface integral extends to both the area covered by the epilayer ($X_3=0$), and to the external boundary of the substrate not covered by the epilayer. The latter leads to the familiar traction-free boundary condition, and will be excluded from the subsequent discussion.

We can treat the surface energy variation in (10) in a similar manner. Using (6), (7) and (9), we obtain that

$$\begin{aligned} \int \delta \Gamma \, dA &= \int [-(\chi - \xi_{\beta, \beta}) \delta I_\alpha + \xi_\alpha \delta C + f_{\alpha\beta} \delta u_\beta] m_\alpha \, dL \\ &+ \int [(\chi - \xi_{\beta, \beta})_{,\alpha} \delta I_\alpha - f_{\alpha\beta, \beta} \delta u_\alpha] \, dA. \end{aligned} \quad (12)$$

We will use a periodic boundary condition so that the line integral in the above disappears.

The sum (11) and (12) gives the total energy variation with the variations $\delta \mathbf{u}$ and $\delta \mathbf{I}$:

$$\delta G = \int [(\chi - \xi_{\beta, \beta})_{,\alpha} \delta I_\alpha + (\sigma_{3\alpha} - f_{\alpha\beta, \beta}) \delta u_\alpha + \sigma_{33} \delta u_3] \, dA - \int \sigma_{ij,j} \delta u_i \, dV. \quad (13)$$

The first integral is over the area covered by the epilayer, and the second over the bulk of the system. When the system reaches equilibrium, the total energy variation vanishes with the variation of the elastic displacements and of the mass displacements. This condition does not guarantee a stable equilibrium state. The stability has to be determined by an energy minimum. We will investigate the stability in the next section.

The system reaches the mechanical equilibrium when the energy variation

vanishes with the elastic displacement variation. According to (13), the mechanical equilibrium requires the field equation in the volume:

$$\sigma_{ij,j} = 0, \quad (14)$$

and the boundary conditions on the surface:

$$\sigma_{3\alpha} = f_{\alpha\beta,\beta} \quad (15a)$$

$$\sigma_{33} = 0. \quad (15b)$$

Eq. (14) recovers the familiar equilibrium equation in elasticity. The boundary conditions in (15) recover those in the work of Freund (1998) and others. They have an intuitive explanation. Fig. 4 illustrates a two-dimensional situation, where the bulk is represented by a plane, and the surface by a straight line. A surface element dx is cut out as a free body. The surface stress f acts like a line tension in the element, and a shear stress σ transmits the interaction between the surface and the bulk substrate. Force balance of the element in the horizontal direction requires that $\sigma = df/dx$, which is a special case of the more general equation (15a). Force balance in the vertical direction requires that the normal stress vanish, which recovers (15b).

The system reaches the chemical equilibrium when the energy variation vanishes with the mass displacement variation. According to (13), the chemical equilibrium requires that

$$(\chi - \xi_{\beta,\beta}),_{\alpha} = 0. \quad (16)$$

That is, the quantity in the bracket vanishes in the chemical equilibrium.

To summarize, in equilibrium, the elastic field satisfies the usual field equations of elasticity, and the concentration field satisfies (16). Because the surface stresses depend on concentration, the boundary condition (15) couples the elastic field and the concentration field. Eq. (16) also couples the two fields.

As an important special case, consider an epilayer on a semi-infinite substrate.

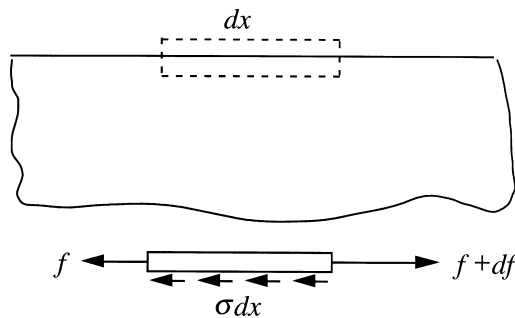


Fig. 4. The interpretation of the boundary condition involving the surface stress.

When the concentration field is uniform in the epilayer, and the strain field vanishes in the bulk, one can confirm readily that all the mechanical and chemical equilibrium conditions are satisfied. Consequently, a uniform epilayer on a strain-free, semi-infinite substrate is an equilibrium state. We will examine the stability of this equilibrium state in later sections.

4. Nonequilibrium thermodynamics

As stated above, once the constraint of uniform concentration is removed, the system can further relax by making two kinds of adjustments: elastic distortion and species relocation. The two adjustments occur at vastly different time scales. Elastic distortion is a much faster process than species relocation. The former is mediated by elastic waves, and the latter by atomic diffusion. Consequently, the mechanical equilibrium is taken to be maintained at all times, during which atomic diffusion proceeds to relax the system.

When the system is not in chemical equilibrium, the energy variation does not vanish with mass displacement variation, so that (16) is no longer valid. Define the driving force F_α for diffusion as the reduction of the total energy per atom relocating per unit distance. Thus,

$$\int F_\alpha \delta I_\alpha \, dA = -\delta G. \quad (17)$$

Comparing (17) and (13) in mechanical equilibrium, we find that

$$F_\alpha = -(\chi - \xi_{\beta, \alpha}), \quad (18)$$

As expected, the driving force exists when the system is not in chemical equilibrium.

Define a vector field \mathbf{J} (called the flux), such that $J_\alpha m_\alpha$ is the number of A atoms across a unit length of the curve on the surface per unit time. Following the linear nonequilibrium thermodynamics (Callen, 1985), we assume that the flux is linearly proportional to the driving force:

$$J_\gamma = M_{\gamma\alpha} F_\alpha, \quad (19)$$

where $M_{\gamma\alpha}$ are the mobilities of atoms, and form a symmetric and positive-definite tensor. Cahn (1961) used a similar kinetic law to model spinodal decomposition in bulk crystals.

The conservation of the occupied sites requires that the time rate of the concentration compensate the divergence of the flux vector, namely,

$$\partial C / \partial t = -J_{\alpha, \alpha}. \quad (20)$$

One can evolve the system by updating the strain and the concentration field with time. At a given time, knowing the concentration field, one determines the elastic

field by solving the standard elasticity field equations, subject to the boundary conditions (15). Once the strain fields are determined, one calculates the driving force from (18) and the flux field from (19). One then updates the concentration field according to (20) for a time step. The whole procedure repeats itself for the next time step. This dynamical system can be used to simulate the emergence and evolution of the phase pattern in a similar way as in bulk alloys (Chen and Wang, 1996). Following Suo (1997), we can readily formulate a weak statement for the evolution process. These matters will not be pursued in this paper, because we will focus on the stability of the uniform epilayer, rather than the evolution of a nonuniform epilayer. The results along the latter line will be reported in a subsequent paper.

5. Surface stress, deformable substrate, and nonuniform concentration

As discussed before, a uniform epilayer on a strain-free, semi-infinite substrate is an equilibrium state. The stability of this equilibrium state is considered in this and the next section. The substrate is taken to be isotropic and linearly elastic, with Young's modulus E and Poisson's ratio ν . The corresponding elastic energy density function is (Timoshenko and Goodier, 1970)

$$W = \frac{E}{2(1+\nu)} \left[\epsilon_{ij}\epsilon_{ij} + \frac{\nu}{1-2\nu} (\epsilon_{kk})^2 \right]. \quad (21)$$

The superficial object is taken to be isotropic in its plane. We will discuss the small perturbation from a uniform concentration field, so that both the concentration-gradient and the strain are small. The concentration itself, however, can take a finite value. Expressed in the leading terms of the concentration-gradient and the strain in the Taylor expansion, the surface energy density is

$$\Gamma = g(C) + h(C)C_{,\alpha}C_{,\alpha} + f(C)\epsilon_{\alpha\alpha}. \quad (22)$$

As indicated, the coefficients g , h and f depend on the concentration, but not on the concentration gradient or the strain. The first term is the surface energy density when the epilayer is uniform, and the substrate is unstrained. This term includes the contributions of all kinds of superficial misfit, as well as the entropy of mixing. The second term is the contribution of the concentration-gradient, which is analogous to that in the Cahn–Hilliard (1958) theory of spinodal decomposition of bulk crystals. The third term is the contribution when the bulk of the system is strained; the coefficient f is analogous to the surface stress of an elemental crystal, as mentioned above. Here we have assumed that the epilayer is isotropic, so that h and f are described with numbers, instead of second-rank tensors. The above expression has neglected the linear term in the concentration-gradient, because the isotropy precludes such a term to contribute to the free energy. The expression has also neglected terms quadratic in strains; this is equivalent to saying that the superficial object has a similar elastic modulus as the

substrate, so that the bulk strains give no excess surface elastic energy. This should be a reasonable approximation. The excess superficial elasticity can be easily added to the theory, but will not be considered in this paper.

We now consider the qualitative effects of various terms on epilayer demixing. We need to compare the total energy G of the uniform epilayer with that of a nonuniform epilayer, keeping the number of each species constant. Imagine now that the system is so constrained that the bulk is strain-free. This is accomplished conceptually by applying surface shear traction to negate the effects of the surface stress gradient (15); an illustration will be given shortly. The first term in (22) contributes in a usual way. If $g(C)$ is convex down, the nonuniformity in the concentration increases the total energy, and this energy term favors a uniform epilayer. If $g(C)$ is convex up, the nonuniformity in the concentration decreases the total energy, and this energy term favors a nonuniform epilayer. The coefficient $h(C)$ is taken to be positive, so that the concentration-gradient by itself always favors a uniform epilayer, motivating phases to coarsen.

We now come to the crux of the matter: the role of the surface stress. If the substrate is rigid, the third term in (22) vanishes even when the composition is nonuniform. If the concentration in the epilayer is uniform, the surface stress is also uniform, so that the substrate is strain-free and the third term in (22) also vanishes. Consequently, the surface stress can vary the total energy when (a) the substrate is deformable, (b) the epilayer is nonuniform, and (c) the surface stress depends on the concentration.

We now explain qualitatively why the substrate deformation allows the nonuniform surface stress to reduce the total energy. The following explanation was used by Pompe et al. (1993) for an analogous situation of a ferroelastic film on a substrate. For now, disregard the concentration and gradient effects, and focus on surface stress nonuniformity by itself. Fig. 5 illustrates a simple two-dimensional case. The surface stress is f_0 everywhere except for the portion of the

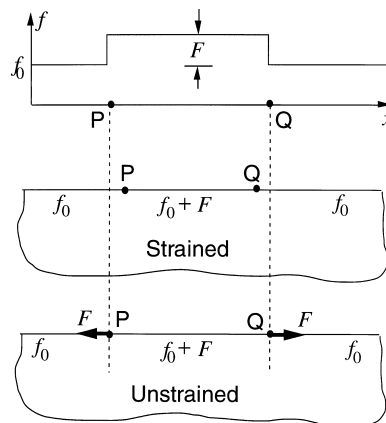


Fig. 5. Bulk deformation allows the nonuniform surface stress to reduce total energy.

surface between points P and Q, where the surface stress steps up by F . The nonuniformity causes the points P and Q to move toward each other, giving rise to a strain field in the bulk. Next imagine that a pair of forces are applied to move the points P and Q away from each other. When the applied forces reach the magnitude F , the bulk becomes unstrained. Because the forces do work to the body, the unstrained state has a higher energy than the strained state. The energy change depends only on F , but not on f_0 . Whether the overall surface stress f_0 is tensile, compressive, or vanishing does not make any difference to the energy reduction.

The same conclusion can be reached more formally as follows. When the surface stress is nonuniform, as shown in the previous section, a shear stress field is induced in the bulk near the surface. When the surface stress is isotropic, (15) specializes to

$$\sigma_{31} = \partial f / \partial x_1, \quad \sigma_{32} = \partial f / \partial x_2, \quad \sigma_{33} = 0. \quad (23)$$

These are the boundary conditions to set up the elastic field in the semi-infinite bulk.

The bulk elastic energy equals the work done by the shear stresses through the displacements on the surface. When the energy density function W is quadratic in the strains, such as that given by (21), this work is given by

$$\int W \, dV = \frac{1}{2} \int \sigma_{3\alpha} u_\alpha \, dA. \quad (24)$$

The nonuniform surface stress also changes the third term in (22). Thus,

$$\int f \epsilon_{\alpha\alpha} \, dA = \int f u_{\alpha, \alpha} \, dA = \int [(f u_\alpha)_{, \alpha} - (f_{, \alpha} u_\alpha)] dA.$$

The divergence theorem transforms the first term in the bracket to an integral over the boundary of the epilayer, which is taken to be so far away and is ignored. The second term in the bracket, upon inserting (23), becomes

$$\int f \epsilon_{\alpha\alpha} \, dA = - \int \sigma_{3\alpha} u_\alpha \, dA. \quad (25)$$

Consequently, the deformation allows the nonuniform surface stress to increase bulk energy (24) and reduce the surface energy (25). The net result is a reduction in the total energy:

$$\int W \, dV + \int f \epsilon_{\alpha\alpha} \, dA = - \frac{1}{2} \int \sigma_{3\alpha} u_\alpha \, dA. \quad (26)$$

Consequently, a concentration-dependent surface stress by itself favors a non-uniform epilayer. Equation (26) is the same as stated in Alerhand et al. (1998).

6. Stability of a uniform epilayer against small perturbation

To examine the stability of a uniform epilayer on a semi-infinite substrate, compare the energy of two states of the system. In the first state, the epilayer has a uniform concentration field, C_0 , and the bulk of the system is strain-free. The last two terms in (22) vanish. The total energy per unit area is $g(C_0)$.

In the second state, the concentration field is perturbed from C_0 with a small amplitude q and an arbitrary wavelength λ . Because of the isotropy, the energy of the perturbed system is independent of the direction of the wave vector. Let the direction of the wave vector coincide with the x_1 -axis, and write the perturbed concentration field as

$$C(x_1, x_2) = C_0 + q \sin\left(\frac{2\pi x_1}{\lambda}\right). \quad (27)$$

Only the sin-component need be considered, because the cos-component represents a translation of the origin of the x_1 -axis, which does not alter the energy in the perturbed state.

Now examine the three terms in (22) in turn. Expand $g(C)$ into the Taylor series around C_0 . A straightforward calculation gives the contribution of $g(C)$ to the energy per unit area:

$$\frac{1}{\lambda} \int_0^\lambda g(C) dx_1 = g(C_0) + \frac{q^2}{4} \left(\frac{d^2 g}{dC^2} \right). \quad (28)$$

Because a change in the sign of q makes no difference to the energy, the term linear in q makes no contribution, and the leading term in q is quadratic. The second derivative $d^2 g/dC^2$ is evaluated at C_0 . As expected, the g -term by itself increases the energy if $d^2 g/dC^2 > 0$. The energy of mixing does not favor any particular wavelength.

The concentration-gradient term in (22) contributes to the energy per area by

$$\frac{1}{\lambda} \int_0^\lambda h(C) C_{,1}^2 dx_1 = \frac{q^2}{2} \left(\frac{2\pi}{\lambda} \right)^2 h(C_0). \quad (29)$$

So long as $h > 0$, the gradient term by itself always increases the energy when the composition modulates. The gradient term penalizes perturbations of short wavelengths, and therefore motivates phases to coarsen.

We now examine the effect of the surface stress f . To the leading order in q , the boundary condition (23) becomes

$$\sigma_{31} = q \left(\frac{df}{dC} \right) \left(\frac{2\pi}{\lambda} \right) \cos\left(\frac{2\pi x_1}{\lambda}\right), \quad \sigma_{32} = 0, \quad \sigma_{33} = 0. \quad (30)$$

The slope df/dC is evaluated at C_0 . The elastic field in the half space subject to the boundary conditions in (30) can be solved analytically (Timoshenko and

Goodier, 1970). This is a plane strain problem. Linearity and dimensional consideration dictate that the displacement field on the surface take the form

$$u_1 = \beta \frac{1 - \nu^2}{E} q \left(\frac{df}{dC} \right) \cos \left(\frac{2\pi x_1}{\lambda} \right), \quad u_2 = 0, \quad (31)$$

where β is a pure number. The exact elasticity solution gives $\beta = 2$. The elastic field in the substrate decays exponentially in the x_3 -direction. Substituting (30) and (31) into (26), we find the energy per unit area due to the surface stress:

$$-\frac{1}{2\lambda} \int_0^\lambda \sigma_{31} u_1 \, dx_1 = -\frac{(1 - \nu^2) q^2}{2E} \left(\frac{2\pi}{\lambda} \right) \left(\frac{df}{dC} \right)^2. \quad (32)$$

As concluded before, the nonuniform surface stress by itself always reduces the energy. Furthermore, it is the slope df/dC , rather than the surface stress, that causes the energy reduction. The sign of df/dC makes no difference to the energy change. As expected, (32) favors perturbations of short wavelengths, and therefore tends to refine phases.

A sum of (28), (29), and (32) gives the net difference in the energy per unit area between the perturbed and the unperturbed state:

$$G - g(C_0) = \frac{q^2}{2} \left[\frac{1}{2} \left(\frac{d^2 g}{dC^2} \right) - \frac{1 - \nu^2}{E} \left(\frac{df}{dC} \right)^2 \left(\frac{2\pi}{\lambda} \right) + h \left(\frac{2\pi}{\lambda} \right)^2 \right]. \quad (33)$$

If perturbation of a given wavelength increases the energy, the uniform epilayer is stable against this perturbation. At a very long wavelength, the first term in the bracket dominates, so that the stability of the uniform epilayer requires that $d^2 g/dC^2 > 0$. At very short wavelength, the third term dominates, so that the stability of the uniform epilayer requires that $h > 0$. At intermediated wavelengths, the df/dC term becomes important and favors a nonuniform epilayer.

If the uniform state has a lower energy than the perturbed state for all wavelengths, the system is stable against all forms of small perturbation. Note that (33) is quadratic in the wavenumber $2\pi/\lambda$. Consequently, the energy change is always positive if, in addition to $h > 0$ and $d^2 g/dC^2 > 0$, the following condition is satisfied:

$$2h \frac{d^2 g}{dC^2} > \left(\frac{1 - \nu^2}{E} \right)^2 \left(\frac{df}{dC} \right)^4. \quad (34)$$

This is the condition for an epilayer of uniform concentration C_0 to be stable against small perturbation in the concentration field. The quantities $d^2 g/dC^2$, df/dC and h are all evaluated at concentration C_0 .

To gain some quantitative feel, let us return to (33), and examine a special case where the gradient-term is negligible (i.e., $h = 0$). When $d^2 g/dC^2 > 0$, the uniform epilayer is unstable for short wavelengths, but stable for long wavelengths. The

critical wavelength is given by

$$\lambda_1 = \frac{4\pi(1 - \nu^2)(df/dC)^2}{E d^2g/dC^2}. \quad (35)$$

In (35), the unit for C can be arbitrary, so long as it is the same for the denominator and the numerator. Here we will use the unit of the number fraction of A atoms in the epilayer. Surface stress has been determined experimentally for several systems by measuring the change in the wafer curvature as atoms are being deposited (Ibach, 1997). A representative magnitude for the slope is $|df/dC| = 1\text{N/m}$, corresponding to a residual stress 10^{10} N/m^2 in a layer 10^{-10} m thick.

For A and B atoms on substrate S, the entropy of mixing gives a miscible alloy at a high temperature. At a low temperature, if like atoms favor like atoms as neighbors, phase separation occurs. We assume that the superficial mixture is a regular solution with

$$\frac{d^2g}{dC^2} = \frac{4k_B}{A_0}(T - T_0) \quad (36)$$

at $C = 0.5$. Here k_B is Boltzmann's constant, A_0 the area per site on the surface, T the temperature of the system, and T_0 is a given quantity. The value of T_0 is specific to the epilayer, which may not be the same as the spinodal temperature for the bulk of the same composition. In the absence of the surface stress effect, when $T > T_0$, the two elements in the epilayer is miscible.

In the presence of the surface stress, without the gradient energy, the uniform epilayer is unstable at short wavelengths. Using the magnitudes $E/(1 - \nu^2) = 10^{11}\text{ N/m}^2$, $A_0 = 10^{-20}\text{ m}^2$, $df/dC = 1\text{N/m}$, and keeping only the order-of-magnitude, we find that the critical wavelength

$$\lambda_1 \cong \frac{100}{T - T_0}, \quad (37)$$

where the units for the temperature and the wavelength are K and nm. For example, when $T - T_0 = +10\text{ K}$, the epilayer would be miscible in the absence of the surface stress effect; however, due to the concentration-dependent surface stress, a uniform epilayer is unstable for wavelengths below about 10 nm.

We can also discuss the special case where the first term in the bracket in (33) is negligible, so that the second and the third term compete. The uniform epilayer is stable for short wavelengths, but unstable for long wavelengths. The critical wavelength is given by

$$\lambda_2 = \frac{2\pi Eh}{(1 - \nu^2)(df/dC)^2}. \quad (38)$$

The surface stress slope df/dC tends to refine the structure. This why the surface-stabilized phases resist coarsening caused by the gradient energy.

We may compare our model with that of Glas (1987). He considered the effect of elastic misfit on a flat binary semiconductor film. He assumed that the total free energy is the sum of elastic energy and composition-dependent energy (chemical energy), both being treated as bulk volumetric energy. He considered the case where (i) the film lattice constant matches with that of the substrate when the film concentration is uniform, and (ii) the chemical energy drives phase separation when the film is unconstrained. When the film concentration is uniform, the elastic energy vanishes, but the chemical energy is high. When the film concentration undulates, the film-substrate composite acquires elastic energy, but the chemical energy is reduced. Consequently, the elastic energy favors a uniform film, and tends to reduce the phase separation temperature.

In this paper, we assume that the free energy is the sum of the volumetric energy and the superficial energy, Eq. (4). The superficial energy density consists of three terms, as in Eq. (22). These terms formally correspond to terms in the Glas model. The surface stress corresponds to the residual stress in the film. The term $g(C)$ corresponds to the chemical energy plus elastic energy, holding strain constant. Glas did not include the effect of concentration gradient. Although a mathematical comparison of the two models may be made, we will not pursue it here. As mentioned in the Introduction, the measured surface stress can be several times that predicted based on lattice misfit. Consequently, such a mathematical comparison may have little practical value, so far as thin epitaxial layers are concerned.

7. Concluding remarks

This paper studies demixing behaviors of a binary epilayer. We regard the epilayer and the adjacent substrate monolayers as a single superficial object, and define the excess surface energy for this object. Consequently, the surface energy includes the effects of entropy of mixing and various kinds of superficial misfit. The bulk strain effect is included in the regular elastic energy. We prescribe an explicit form for the surface energy as a function of concentration, concentration-gradient, and strain. The mechanical equilibrium is maintained at all times, but the chemical equilibrium is not. Atoms diffuse to reach the chemical equilibrium. A stability analysis is given, where a uniform concentration is perturbed into a sinusoidal profile of a small amplitude and an arbitrary wavelength, and the energy change is calculated to the quadratic term of the perturbation amplitude. The composition-dependent surface stress tends to refine phases, resisting coarsening. We identified the condition under which a uniform epilayer is stable against perturbations of all wavelengths. In a subsequent paper we will report on a study of evolving concentration field and pattern formation using the dynamical system developed here.

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