SELF-ORGANIZING NANOPHASES ON A SOLID SURFACE

Z. SUO and W. LU

Mechanical and Aerospace Engineering Department
and Materials Institute
Princeton University, Princeton, NJ 08544

Prepared for a book dedicated to
Professor James R. Rice
on the occasion of his 60th birthday

Edited by T.-J. Chuang
To be published by Kluwer Academic Publishers in 2000

SELF-ORGANIZING NANOPHASES ON A SOLID SURFACE

Z. SUO and W. LU
Mechanical and Aerospace Engineering Department and Materials Institute
Princeton University, Princeton, NJ 08544

Abstract

A two-phase epilayer on a substrate may exhibit intriguing behaviors. The phases may select stable sizes, often on the order of 10 nm. The phases sometimes order into a periodic pattern, such as alternating stripes or a lattice of disks. The patterns may be stable on annealing. This paper describes a model that accounts for these behaviors. The phase boundary energy drives phase coarsening. The concentration-dependent surface stress drives phase refining. The competition stabilizes nanoscopic phases and periodic patterns.

1. Introduction

Rice and co-workers wrote a series of papers on polycrystalline materials subject to both stress and heat (Chuang and Rice, 1973; Chuang *et al*., 1979; Needleman and Rice, 1980; Rice and Chuang, 1981). The phenomenon concerned a cavity on a grain boundary. The cavity could change shape and size via mass transport processes (creep, diffusion on the cavity surface, and diffusion on the grain boundary), driven by thermodynamic forces (stress, surface energy, and grain boundary energy). Building on those of Herring (1951), Mullins (1957), and Hull and Rimmer (1959), the papers developed a general approach to this complex phenomenon.

Figure 1 outlines the approach in generic terms. The basic ingredients are kinematics, energetics, and kinetics. To model an evolving structure, one first describes its configuration with kinematic quantities: the shape of the structure, the deformation field, the concentration field, etc. These kinematic quantities are thermodynamic coordinates. One then equips the structure with a free energy as a functional of the kinematic quantities. The variation of the free energy associated with the variation of the kinematic quantities defines the driving force. Finally one provides the kinetic relations between the rate of the kinematic quantities and the driving forces.

These ingredients are combined into a variational statement. Depending on the type of the kinematic quantities, the variational statement ramifies into several routes to simulate the evolution of the structure. If the kinematics comprises fields, the variational statement leads to partial differential equations and boundary conditions. If the kinematics comprises discrete variables, the variational statement leads to ordinary differential equations. If the structure is divided into elements, the variational statement leads to a finite element model.

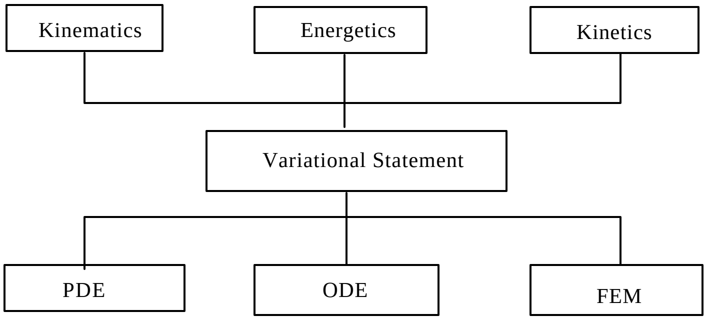


Figure 1. A general approach to evolving structures.

In the world of dissipative, time-dependent phenomena, this approach has a long tradition, dating back to the treatment of damped vibration by Rayleigh (1894), irreversible thermodynamics by Prigogine (1967) and others, spinodal decomposition by Cahn and Hilliard (1958), and heat transfer by Biot (1970). The approach has been extended to study diverse material structures (e.g., Khachaturyan, 1983; Srolovitz, 1989; McMeeking and Kuhn, 1992; Gao, 1994; Freund, 1995; Suo, 1997; Carter *et al.*, 1997; Bower and Craft, 1998; Cocks *et al*., 1999). Recent applications include self-assembled quantum dots, electromigration voids, ferroelectric domains, and emerging crack tips; see reviews by Freund (2000) and Suo (2000). Like other fields to which Rice has made seminal contributions, this field has advanced solid mechanics by submitting it to the challenge of significant phenomena.

2. Self-Organization by Competitive Coarsening and Refining

This paper considers a particular phenomenon: self-organized nanophases in binary epilayers. For a decade high-resolution imaging techniques, such as Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM), have spurred intense studies of nanoscopic activities on solid surfaces. Kern *et al*. (1991) deposited a submonolayer of oxygen on a copper (110) surface. On annealing, the oxygen atoms arranged into stripes that alternate with bare copper stripes. The width of the stripes was on the order of 10 nm. The self-assembled nanostructure can be a template for making functional structures. Li *et al*. (1999) grew ferromagnetic iron films on the oxygen-striped copper substrate. The stripe structure was retained up to several monolayers of the iron films. Periodic patterns have also been observed in other material systems. Pohl *et al*. (1999) deposited a monolayer of silver on a ruthenium (0001) surface, and then exposed the silver-covered ruthenium to sulfur. The epilayer became a composite of sulfur disks in a silver matrix. The sulfur disks were of diameter about 3.4 nm, and formed a triangular lattice.

The observations include nanoscopic phases, periodic patterns, and stability on annealing. These behaviors are intriguing because they are absent in bulk phase separation. The basic behaviors of bulk phase separation are well known. Below a critical temperature, a miscible solution becomes unstable and separate into two phases. One phase may form particles, and the other a continuous matrix. In the beginning, the particles are small and the total area of the phase boundaries is large. The atoms at the phase boundaries have excess free energy. To reduce the free energy, the total area of the phase boundaries must reduce. Consequently, atoms leave small particles, diffuse in the matrix, and join large particles. Over time the small particles disappear, and the large ones become larger. The process is known as *phase coarsening*. Time permitting, the phases will coarsen until only one big particle left in the matrix.

The two phases usually have different atomic lattice constants. If the phase boundaries are coherent, the lattice constant misfit induces an elastic field. For simplicity, assume that both phases have cubic atomic lattices, with lattice constants a_1 and a_2, respectively. The misfit strain is $e_M = (a_1 - a_2)/a_1$. Let E be an elastic modulus. The elastic energy per unit volume scales as Ee_M^2, invariant with the average particle size. Consequently, *bulk elastic misfit does not stop phase coarsening*.

In the preceding paragraph, we have excluded other size scales of the system. Imagine, for example, a thin film bonded to a substrate. The film undergoes phase separation, but the substrate does not. The film thickness provides a length scale. When the particle size approaches and exceeds the film thickness, the total elastic energy of the system increases with the particle size in the lateral direction (Roytburd, 1993; Pompe *et al*. 1993). Consequently, the elastic energy in the film-substrate composite causes *phase refining*. The two competing actions—refining due to elasticity and coarsening due to phase boundaries—can select an equilibrium phase size. Similar competing actions are well known in ferroelectric films and polycrystals; see Suo (1998) for review. In the latter, the grain size provides the needed length scale. Long range interactions other than elasticity, such as electrostatics, can also refine phases (Chen and Khachaturyan, 1993; Ng and Vanderbilt, 1995).

This mechanism may account for composition modulation sometimes observed in multi-component semiconductor films, although we cannot be certain until a detailed model is developed and compared with experimental observations. The existing models (Glas, 1997; Guyer and Voorhees, 1998) do not include the film thickness effect, so they do not have the ingredient of phase refining. It would be significant to see if the model with both coarsening and refining actions can stabilize composition modulation.

The instability of self-assembled quantum dots provides another case study; see Freund (2000) for review. Imagine an elemental semiconductor film on another elemental semiconductor substrate, such as germanium film on silicon substrate. The misfit lattice constants of the two crystals induce an elastic field, assuming that the interface is coherent. The film may break into islands to reduce the elastic energy. The shape change is via atomic diffusion on the surface. It is sometimes observed that the islands have a narrow size distribution, and even order into periodic patterns. Nonetheless we note that in this case elasticity cannot stop coarsening. Surface diffusion allows the islands to change both lateral size and height. For example, if the islands coarsen with a self-similar shape, the average elastic energy is invariant with the island size. Should stable periodic islands ever be observed, something in addition to classical elasticity must be invoked to stop coarsening.

3. A Model of a Binary Eiplayer on a Substrate

From the above discussion, it is clear that a model of self-organizing phases should contain the following ingredients: phase separation, phase coarsening, and phase refining. Each ingredient may be given alternative mathematical and physical representations. We next summarize a model proposed by Suo and Lu (2000).

Imagine an epilayer of two atomic species A and B on a substrate of atomic species S. The epilayer is one atom thick, and the substrate occupies the half space $x_3 < 0$, bounded by the x_1-x_2 plane. The two species A and B can be both different from that of the substrate (such as sulfur-silver on ruthenium). Alternatively, only one species of the epilayer is different from that of the substrate (such as oxygen on copper). The epilayer is a substitutional alloy of A and B. Atomic diffusion is restricted within the epilayer.

3.1 KINEMATICS

Two sets of kinematic quantities describe the configuration of the epilayer-substrate composite: one for elastic deformation, and the other for mass transport. Let u_i be the displacements in the substrate. A Latin subscript runs from 1 to 3. We assume that the epilayer is coherent on the substrate. When the substrate deforms, the epilayer deforms by the same amount as the substrate surface. Consequently, the displacement field of the substrate completely specifies the deformation state of the epilayer-substrate composite. The misfit strains in the epilayer remain constant, and therefore need not be explicitly represented as a thermodynamic variable.

Let C be the fraction of atomic sites on the surface occupied by species A. Imagine a curve on the surface. 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 lying in the surface normal to the curve by $\boldsymbol{m}$. Define a vector field $\boldsymbol{I}$ in the surface (called the mass relocation), such that $I_\alpha m_\alpha$ is the number of A-atoms across a unit length of the curve. A Greek subscript runs from 1 to 2. A repeated index implies summation. Mass conservation requires that the variation in the concentration relate to the variation in the mass relocation as

$$\Lambda \delta C = -\delta I_{\alpha,\alpha}\,, \tag{1}$$

where Λ is the number of atomic sites per unit area. Similarly define a vector field $\boldsymbol{J}$ (called the mass 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. The relation between $\boldsymbol{I}$ and $\boldsymbol{J}$ is analogous to that between displacement and velocity. The time rate of the concentration compensates the divergence of the flux vector, namely,

$$\Lambda \partial C / \partial t = -J_{\alpha,\alpha}\,. \tag{2}$$

3.2 ENERGETICS

We next specify the free energy as a functional of the kinematic quantities u_i and C. Let the reference state for the free energy be atoms in three unstrained, infinite, pure crystals of A-atoms, B-atoms and S-atoms. When atoms are taken from the reference state to form the epilayer-substrate composite, the free energy changes, due to the entropy of mixing, the misfits among the three kinds of atoms, and the presence of the free space. In addition, the misfits can induce an elastic field in the substrate. Let G be the free energy of the entire composite relative to the same number of atoms in the reference state. For an epilayer only one atom thick, we cannot attribute the free energy to individual kinds of misfit. Instead, we lump the epilayer and the adjacent monolayers of the substrate into a single superficial object, and specify its free energy. The free energy of the composite consists of two parts: the bulk and the surface, namely,

$$G = \int W dV + \int \Gamma dA . \tag{3}$$

The first integral extends over the volume of the entire system, W being the elastic energy per unit volume. The second integral extends over the surface area, Γ being the surface energy per unit area. Both the volume and the surface are measured in the unstrained substrate. As a convention, we extend the value of the substrate elastic energy W all the way into the superficial object. Consequently, the surface energy Γ is the excess free energy in the superficial object in addition to the value of the substrate elastic energy. The convention follows the one that defines the surface energy for a one-component solid.

The elastic energy per unit volume, W, takes the usual form, being quadratic in the displacement gradient tensor, $u_{i,j}$. We assume that the substrate is isotropic, with Young's modulus E and Poisson's ratio n. The elastic energy density function is

$$W = \frac{E}{2(1+n)}\left[u_{i,j}u_{i,j} + \frac{n}{1-2n}\left(u_{kk}\right)^2 \right]. \tag{4}$$

The stresses s_{ij} are the differential coefficients, namely, $dW = s_{ij} du_{i,j}$.

The surface energy per unit area, Γ, takes an unusual from, as we now explain. Assume that Γ is a function of the concentration C, the concentration gradient $C_{,a}$, and the displacement gradient in the surface, $u_{a,b}$. Expend the function $\Gamma\left(C, C_{,a}, u_{a,b}\right)$ to the leading order terms in the concentration gradient $C_{,a}$ and the displacement gradient $u_{a,b}$:

$$\Gamma = g + hC_{,b}C_{,b} + f u_{b,b} , \tag{5}$$

where g, f and h are all functions of the concentration C. We have assumed isotropy in the plane of the surface; otherwise both f and h should be replaced by second rank tensors. The leading order term in the concentration gradient is quadratic because, by symmetry, the term linear in the concentration gradient does not affect the surface energy. We have neglected terms quadratic in the displacement gradient tensor, which relate to the excess in the elastic constants of the epilayer relative to the substrate. We next explain the physical content of (5) term by term.

When the concentration field is uniform in the epilayer, the substrate is unstrained, and the function $g(C)$ is the only remaining term in G, the excess free energy of the composite relative to the reference state. Consequently, $g(C)$ is the surface energy per unit area of the uniform epilayer on the unstrained substrate. We assume that the epilayer is a regular solution, so that the function takes the form

$$g(C) = g_{\mathrm{A}}(1 - C) + g_{\mathrm{B}}C + \Lambda kT\left[C \ln C + (1 - C)\ln(1 - C) + \Omega C(1 - C)\right]. \tag{6}$$

Here g_{A} and g_{B} are the excess energy of the superficial object when the epilayer is pure A or pure B. In the special case that A, B and S atoms are all identical, g_{A} and g_{B} reduce to the surface energy of an unstrained one-component solid. Due to mass conservation, the average concentration is constant when atoms diffuse within the epilayer. Consequently, in (6) the terms involving g_{A} and g_{B} do not affect diffusion. Only the function in the bracket does. The first two terms in the bracket result from the entropy of mixing, and the third term from the energy of mixing. The dimensionless number Ω measures bond strength relative to the thermal energy kT. When $\Omega < 2$, the function is convex. When $\Omega > 2$, the function is nonconvex. The $g(C)$ function is mainly responsible for phase separation; it favors neither coarsening nor refining.

We assume that $h(C)$ is a positive constant, $h(C) = h_0$. Any nonuniformity in the concentration field by itself increases the free energy Γ. Consequently, the second term in (5) is taken to represent the phase boundary energy; the term drives phase coarsening. The first two terms in (5) are analogous to those in the model of bulk phase separation of Cahn and Hilliard (1958). The model represents a phase boundary by a concentration gradient field. An alternative model would represent a phase boundary by a sharp discontinuity. The merits of the two models have been extensively discussed in the literature, and will not be repeated here.

Now look at the last term in (5), where $u_{1,1}$ and $u_{2,2}$ are the strains in the surface. By definition, f is the change in the surface energy per unit strain. Consequently, f represents the residual stress in the superficial object. More precisely, it is the resultant force per unit length. The quantity f is known as the surface stress (Cahn 1980, Rice and Chuang 1981). The existing literature mainly concerns the surface stress for one-component solids (Cammarata, 1994; Cammarata and Sieradzki,1994; Freund, 1998; Gurtin and Murdoch, 1975; Willis and Bullough, 1969; Wu, 1996). In the present problem, when the concentration is nonuniform, the surface stress is also nonuniform, and induces an elastic field in the substrate. As stated in Section 2, such an elastic field will refine phases. For simplicity, we assume that the surface stress is a linear function of the concentration, $f(C) = f_0 + f_1 C$. Ibach (1997) has reviewed the experimental information on this function. Surface energy can also be a function of an order parameter. Alerhand *et al*. (1988) used the idea to model surface domain patterns.

3.3 KINETICS

The composite evolves by making two kinds of changes: elastic deformation in the substrate, and mass relocation in the epilayer. Elastic deformation does not dissipate energy, but mass transport does. Define the driving force F_a as the reduction of the free energy of the composite when an atom relocates by unit distance. Following Cahn (1961), we specify a kinetic law by relating the atomic flux linearly to the driving force:

$$J_a = MF_a \,, \tag{7}$$

where M is the mobility of atoms in the epilayer. Again we have assumed isotropy in the surface; otherwise M should be replaced by a second rank tensor.

4. Variational Statement and Partial Differential Equations

We now mix the ingredients. Recall that the driving force is defined as the reduction of the free energy of the composite when an atom relocates by unit distance. Translating this definition into a mathematical description, we have

$$\int F_a dI_a \, dA = -dG \,. \tag{8}$$

The two vector fields, ***u*** and ***I***, are basic kinematic variables; they vary independently, subject to no constraint. Mass transport dissipates energy, but elastic deformation does not. The variational statement (8) embodies these considerations.

Calculate dG using the equations in Section 3, giving

$$\begin{aligned} dG = \int \left[\frac{1}{\Lambda} \left(\frac{\P g}{\P C} - 2h_0 \nabla^2 C + f_1 u_{b,b} \right)_{,a} dI_a + \left(s_{3a} - f_{,a} \right) du_a + s_{33} du_3 \right] dA \\ - \int s_{ij,j} du_i \, dV \end{aligned} \tag{9}$$

where $\nabla^2 = \P^2 / x_1^2 + \P^2 / x_2^2$.

Now compare (8) and (9). The free energy variation with the mass relocation gives the expression for the driving force for diffusion:

$$F_a = -\frac{1}{\Lambda} \left(\frac{\P g}{\P C} - 2h_0 \nabla^2 C + f_1 u_{b,b} \right)_{,a} \,. \tag{10}$$

Because elastic deformation does not dissipate energy, the free energy variation with the elastic displacement vanishes, leading to

$$s_{ij,j} = 0 \tag{11}$$

in the bulk and

$$s_{3a} = f_{,a} \,, \qquad s_{33} = 0 \tag{12}$$

on the surface. Equation (11) recovers the equilibrium equation in the elasticity theory. Equation (12) has a straightforward interpretation. Recall that the surface stress is the resultant force (per unit length) of the residual stress in the surface layers. Force balance equates the gradient of the surface stress to the tangential traction. Equation (12) sets the boundary conditions of the elastic field in the substrate.

Observe that the concentration-dependent surface stress varies with both fields ***u*** and ***I***. Consequently, the two fields are coupled, as will be clear shortly. The surface stress enters the diffusion driving force (10), and causes the concentration field to change. Once concentration field changes, the surface stress changes and, through the boundary conditions (12), changes the elastic field in the substrate.

The elastic field in a half space due to a tangential point force acting on the surface was solved by Cerruti (see p. 69 in Johnson, 1985). A linear superposition gives the field due to distributed traction on the surface. Only the expression $u_{\beta,\beta}$ enters the diffusion driving force. The Cerruti solution gives

$$u_{\beta,\beta} = -\frac{\left(1-\nu^2\right)f_1}{\pi E}\iint \frac{\left(\xi_1 - x_1\right)\dfrac{\partial C}{\partial \xi_1} + \left(\xi_2 - x_2\right)\dfrac{\partial C}{\partial \xi_2}}{\left[\left(\xi_1 - x_1\right)^2 + \left(\xi_2 - x_2\right)^2\right]^{3/2}} d\xi_1 d\xi_2 \,. \tag{13}$$

The integration extends over the entire surface.

A combination of (2), (7) and (10) leads to a diffusion equation:

$$\frac{\partial C}{\partial t} = \frac{M}{\Lambda^2}\nabla^2\left(\frac{\partial g}{\partial C} - 2h_0\nabla^2 C + f_1 u_{\beta,\beta}\right). \tag{14}$$

Equations (6), (13) and (14) define the evolution of the concentration field. Once the concentration field is given at $t = 0$, these equations update it for the subsequent time.

Equation (14) looks similar to that of Cahn (1961) for spinodal decomposition. The main difference is how elasticity is introduced. Cahn considered misfit effect caused by composition nonuniformity in the bulk. As discussed in Section 2, such an elasticity effect does not refine phases. Consequently, no stable pattern is expected. Indeed, numerical simulations have shown that the phases coarsen indefinitely, limited only by the computational cell size or computer time; see review by Chen and Wang (1996). By contrast, the elasticity effect in our model comes from nonuniform surface stress, which is similar to the nonuniform residual stress in the thin film discussed in Section 2. This elasticity effect does refine phases.

5. Scales and Parameters

A comparison of the first two terms in the parenthesis in Eqn. (14) sets a length:

$$b = \left(\frac{h_0}{\Lambda kT}\right)^{1/2}. \tag{15}$$

This length scales the distance over which the concentration changes from the level of one phase to that of the other. Loosely speaking, one may call b the width of the phase boundary. The magnitude of h_0 is on the order of energy per atom at a phase boundary, namely, $h_0 \sim 1\,\mathrm{eV}$. Using magnitudes $h_0 \sim 10^{-19}\,\mathrm{J}$, $\Lambda \sim 10^{20}\mathrm{m}^{-2}$ and $kT \sim 10^{-20}\,\mathrm{J}$ (corresponding to $T = 700$ K), we have $b = 0.3$ nm.

The competition between coarsening and refining (i.e., between the last two terms in Eqn. 14) sets another length:

$$l = \frac{Eh_0}{\left(1-n^2\right)f_1^2}. \tag{16}$$

This length scales the equilibrium phase size. Young's modulus of a bulk solid is about $E \sim 10^{11}\mathrm{N/m}^2$. According to the compilation of Ibach (1997), the slope of the surface stress is on the order $f_1 \sim 1\,\mathrm{N/m}$. These magnitudes, together with $h_0 \sim 10^{-19}\,\mathrm{J}$, give $l \sim 10\mathrm{nm}$. This estimate is consistent with the experimentally observed stable phase sizes.

From (14), disregarding a dimensionless factor, we note that the diffusivity scales as $D \sim MkT/\Lambda$. To resolve events occurring over the length scale of the phase boundary width, *b*, the time scale is $t = b^2/D$, namely,

$$t = \frac{h_0}{M(kT)^2}. \tag{17}$$

To resolve events over the length scale of the phase size, *l*, the time scale is $l^2/D = (l/b)^2 t$.

Normalize the coordinates x_a and x_a by *b*, and the time *t* by *t*. In terms of the dimensionless coordinates and time, Eqns. (13) and (14) are combined into

$$\frac{\partial C}{\partial t} = \nabla^2 \left\{ \frac{\partial g}{\partial C} - 2\nabla^2 C - \frac{1}{p}\left(\frac{b}{l}\right) \iint \frac{(x_1 - x_1)\frac{\partial C}{\partial x_1} + (x_2 - x_2)\frac{\partial C}{\partial x_2}}{\left[(x_1 - x_1)^2 + (x_2 - x_2)^2\right]^{3/2}} dx_1 dx_2 \right\}. \tag{18}$$

The system is nonlinear and nonconvex because of the function $g(C)$. The first two terms in (6) disappear after the differentiation in (18). The expression for g in (18), normalized by ΛkT, is

$$g(C) = C\ln C + (1-C)\ln(1-C) + \Omega C(1-C). \tag{19}$$

The problem has two dimensionless parameters: l/b and Ω. The parameter l/b measures the ratio of the equilibrium phase size to the phase boundary width; a representative value is $l/b \sim \sqrt{1000}$. This ratio appears in front of the refining term in (18) as a small parameter. The parameter Ω measures the degree of the convexity of the free energy; $g(C)$ is nonconvex when $\Omega > 2$. Parameters describing the initial concentration field also enter the problem. In so far as the equilibrium pattern is concerned, only the average concentration, C_{ave}, is important. Recall that C_{ave} is time-invariant because of mass conservation.

6. Linear Perturbation Analysis

This section summarizes the results of a linear perturbation analysis (Lu and Suo 1999). As stated before, when the concentration field is uniform, the substrate is unstrained, and the composite is in an equilibrium state. To investigate the stability of this equilibrium state, we superpose to this uniform concentration field a perturbation of a small amplitude. The small perturbation can be represented by a superposition of many sinusoidal components. Consider one such component, which is a sinusoidal field in the x_1 direction. Let C_0 be the uniform concentration from which the system is perturbed, q_0 be the perturbation amplitude at time $t = 0$, and b be the perturbation wavenumber. The wavenumber relates to the wavelength l as $b = 2p / l$. According to the linear perturbation analysis, at time t the concentration field becomes

$$C = C_0 + q_0 \exp(at) \sin bx_1 . \tag{20}$$

Over time, the concentration field keeps the same wavenumber, but changes the amplitude exponentially. The characteristic number a is given by

$$a = -\frac{2}{t}\left(\frac{b}{l}\right)^4 \left[\frac{h}{2} - bl + (bl)^2\right](bl)^2 , \tag{21}$$

with

$$h = \left(\frac{l}{b}\right)^2 \left[\frac{1}{C_0(1-C_0)} - 2\Omega\right]. \tag{22}$$

If $a > 0$, the perturbation amplitude grows exponentially with the time, and a nonuniform epilayer is obtained. If $a < 0$, the perturbation amplitude decays exponentially with the time, and the uniform epilayer is stable.

Figure 2 plots a as a function of the wavelength. We distinguish three cases:

- When $h > 0.5$, $a < 0$ for all wavelengths, so that the uniform epilayer is stable against perturbation of all wavelengths.
- When $h < 0$, the curve intersects with the horizontal axis only at one point, so that the uniform epilayer is stable for short wavelengths, but unstable for long wavelengths.
- When $0 < h < 0.5$, the curve intersects with the horizontal axis at two points, so that the uniform epilayer is stable against perturbations of long and short wavelengths, but unstable against perturbations of an intermediate range of wavelengths. From (22) $0 < h < 0.5$ means that $g(C)$ is convex at C_0, but is very shallow. Acting by itself, $g(C)$ would stabilize the uniform epilayer. In the presence of concentration-

dependent surface stress, however, the shallow convex $g(C)$ is insufficient to stabilize the uniform epilayer.

For a sufficiently small h , the curve reaches a peak at wavelength

$$\frac{l_{\mathrm{f}}}{l} = \frac{16p}{3+\sqrt{9-16h}} . \tag{23}$$

This wavelength corresponds to the fastest growing perturbation mode. The linear perturbation analysis is valid so long as the perturbation amplitude $q_0 \exp(at)$ is small compared to C_0. The results are useful to check numerical simulation. However, the linear perturbation analysis cannot predict the equilibrium pattern, where the concentration nonuniformity has large magnitudes. These considerations will become clear in the next section.

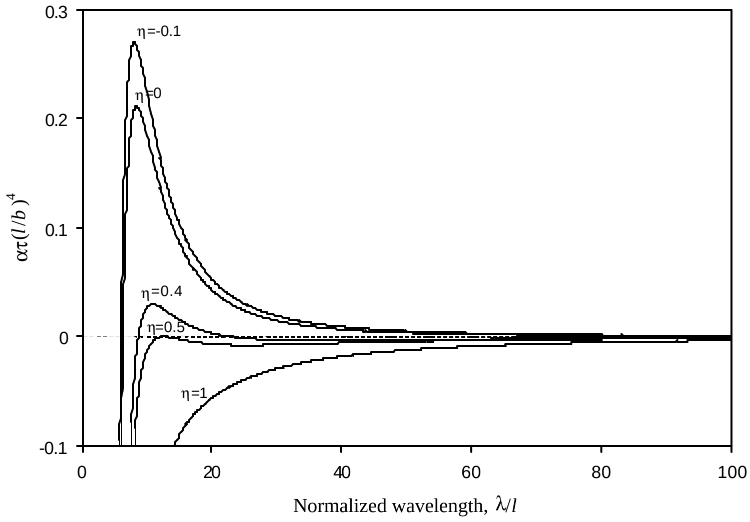


Figure 2 The characteristic number as a function of the wavelength.

7. Numerical Simulation

In numerical simulation, the epilayer is divided into grids. To resolve a phase boundary, the grid size should be smaller than b, and the time step should be smaller than t. Only a finite area of the epilayer is simulated; the infinite epilayer is represented by a periodic boundary condition. To reduce the effect of the boundary condition on the phase pattern, the period simulated should be much larger than l. For the diffusion process to affect events at size scale l, the total time should be on the order of $(l/b)^2 t$. We have also developed program in the reciprocal space, using the semi-implicit time integration

(Chen and Shen, 1998). In addition, without using the diffusion equation, we can minimize the free energy to obtain equilibrium phase patterns.

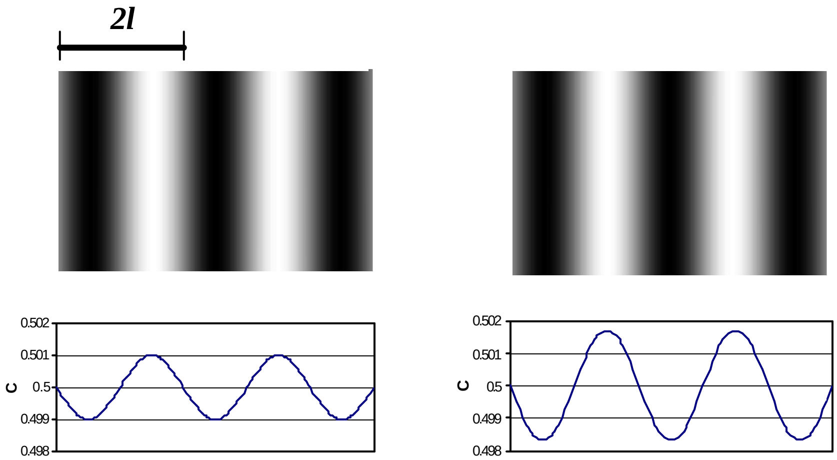
7.1 A SMALL SINUSOIDAL PERTURBATION AS THE INITIAL CONDITION

The parameters in this example are $l / b = \sqrt{1000}$, $\Omega = 2.6$ and $C_{\mathrm{ave}} = 0.5$. The initial concentration perturbation is sinusoidal, with amplitude 10^{-3} and wavelength $2l$. We assume that the concentration field varies with x_1 but not with x_2. Consequently, the diffusion equation is one dimensional, and the substrate is in the state of plane strain deformation. Figure 3 shows the evolving concentration field. The evolution process appears to have three stages. In the first stage, the perturbation amplitude increases with time exponentially, but the wavelength remains constant, as anticipated by the linear perturbation analysis. In the second stage, stripes of a narrow width grow. This new wavelength is selected by the fastest growth mode predicted by the linear stability analysis. For the present parameters, Eqn. (23) gives $l_{\mathrm{f}} / l = 0.35$. In the third stage, the concentration field approaches an equilibrium pattern, with stripe width about l. Energy minimization gives the same equilibrium pattern.

7.2 A LARGE PERTURBATION AS THE INITIAL CONDITION

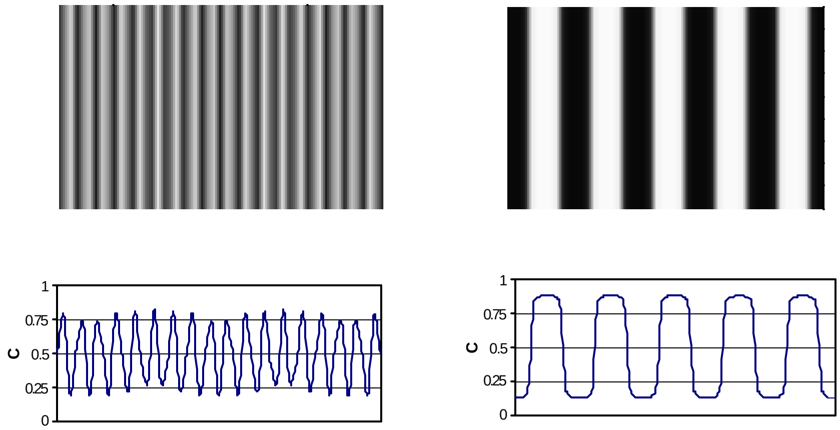
In this example the initial concentration field has a large-amplitude island. All the other parameters are kept the same as before: $l / b = \sqrt{1000}$, $\Omega = 2.6$ and $C_{\mathrm{ave}} = 0.5$. Figure 4 shows the evolving concentration field. The evolution process is very different from that of the previous example, but ends with the same equilibrium pattern.

7.3 PRELIMINARY 2D RESULTS



a. t=0

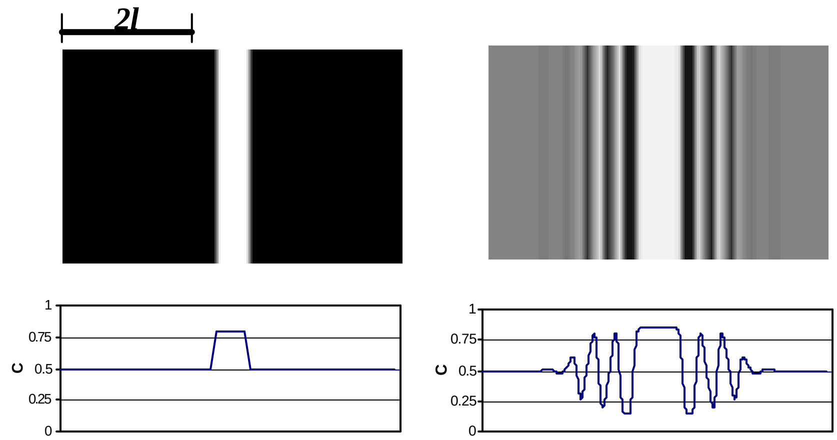
b. t =50τ



c. t=1000τ

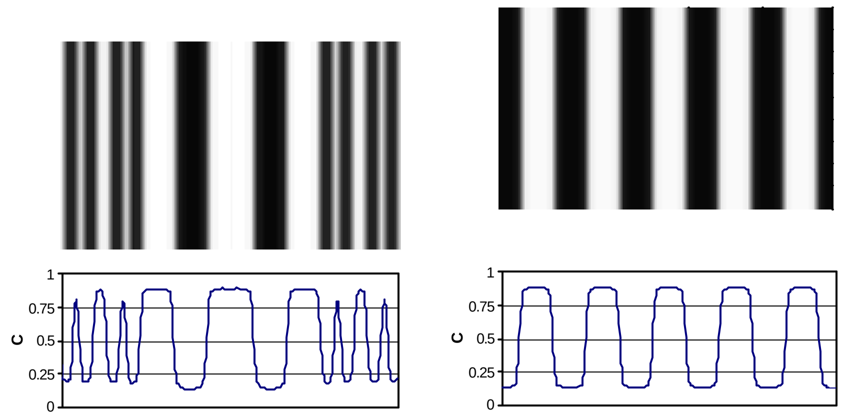
d. t=1.0E5τ

Figure 3 Evolving concentration field. The initial condition is a small perturbation from a uniform field.



a. t=0

b. t=50τ



c. t=1000τ

d. t=1.0E7τ

Figure 4 Evolving concentration field in one dimension. The initial condition is a concentration island.

t=0

t=100τ

t=1000τ

t=1.0E4τ

t=1.0E5τ

t=2.0E5τ

Figure 5 Evolving concentration field in two dimensions

.

8. Conclusion

This paper models a two-phase epilayer on a substrate. The ingredients for ordering a stable, nanoscopic, periodic phase pattern are identified: (1) unstable solid solution for phase separation, (2) phase boundary energy for phase coarsening, and (3) concentration-dependent surface stress for phase coarsening. The concentration-dependent surface stress sets up an elastic field, which is solved by linear superposition using the Cerruti solution. A diffusion equation updates the concentration field. The results of this model available so far are surveyed, including partial differential equations, length and time scales, linear perturbation analysis, and numerical simulation of nonlinear dynamics.

Acknowledgements

This work is supported by the Department of Energy through contract (DE-FG02-99ER45787).

References

Alerhand, O.L., Vanderbilt, D., Meade, R.D., and Joannopoulos, J.D. (1988) Spontaneous formation of stress domains on crystal surfaces. *Phys. Rev. Lett.* **61**, 1973-1976.

Biot, M.A. (1970) *Variational Principles in Heat Transfer*, Oxford University Press, Oxford.

Bower, A.F. and Craft, D. (1998) Analysis of failure mechanisms in the interconnect lines of microelectronic circuits. *Fatigue Fracture Engineering Materials Structure* **21**, 611-630.

Cahn, J.W. (1961) On spinodal decomposition. *Acta Metall.* **9**, 795-801.

Cahn, J.W. (1980) Surface stress and the chemical equilibrium of small crystals—I. the case of the isotropic surface. *Acta Metall.* **28**, 1333-1338.

Cahn, J.W. and Hilliard, J.E. (1958) Free energy of a nonuniform system. I. interfacial free energy. *J. Chem. Phys.* **28**, 258-267.

Carter, W.C., Taylor, J.E., and Cahn, J.W. (1997) Variational methods for microstructural-evolution theories. *JOM*, **49**, No. 12, pp.30-36.

Cammarata, R.C. (1994) Surface and interface stress effects in thin films. *Prog. Surf. Sci.* **46**, 1-38.

Cammarata, R.C. and Sieradzki K. (1994) Surface and interface stresses. Annu. Rev. Mater. Sci. **24**, 215-234.

Chen, L.-Q. and Khachaturyan A.G. (1993) Dynamics of simultaneous ordering and phase separation and effect of long-range coulomb interactions. *Phys. Rev. Lett.* **70**, 1477-11480.

Chen, L.-Q. and Shen J. (1998) Applications of semi-implicit Fourier-spectral method to phase field equations. *Computer Physics Communications* **108**, 14-158.

Chen, L.-Q. and Wang, Y. (1996) The continuum field approach to modeling microstructural evolution. JOM, Vol. **48**, No. 12, pp.13-18.

Chuang, T.-J., Kagawa, K.I., Rice, J.R., and Sills, L.B. (1979) Non-equilibrium models for diffusive cavitation of grain interfaces. *Acta. Metall.* **27**, 265-284.

Chuang, T.-J. and Rice, J.R. (1973) The shape of intergranular creep cracks growing by surface diffusion. *Acta. Metall.* **21**, 1625-1628.

Cocks, A.C.F., Gill, S.P.A., and Pan, J. (1999) Modeling microstructure evolution in engineering materials. *Advances in Applied Mechanics*, **36**, 81-162.

Freund, L.B. (1995) Evolution of waviness on the surface of a strained elastic solid due to stress-driven diffusion. *Int. J. Solids Structures* **32**, 911-923.

Freund, L.B. (1998) A surface chemical potential for elastic solids. *J. Mech. Phys. Solids* **46**, 1835-1844.

Freund, L.B. (2000) The mechanics of electronic materials. *Int. J. Solids Structures*. **37**, 185-196.

Gao, H. (1994) Some general properties of stress-driven surface evolution in a heteroepitaxial thin film structure. *J. Mech. Phys. Solids* **42**, 741-772.

Glas, F. (1997) Thermodynamics of a stressed alloy with a free surface: coupling between the morphological and compositional instabilities. *Phys. Rev.* B **55**, 11277-11286.

Gurtin, M.E. and Murdoch, A.I. (1975) A continuum theory of elastic material surface. *Arch. Rat. Mech. Anal.* **57**, 291-323.

Guyer, J.E. and Voorhees, P.W. (1998) Morphological stability and compositional uniformity of alloy thin films. *J. Crystal Growth* **187**, 150-165.

Herring, C. (1951) Surface tension as a motivation for sintering. *The Physics of Powder Metallurgy*, McGraw-Hill, editor Kingston, W.E., New York pp.143-179.

Hull, D. and Rimmer, D.E. (1959) The growth of grain-boundary voids under stress. *Phil. Mag.*, **4**, 673-687.

Ibach, H. (1997) The role of surface stress in reconstruction, epitaxial growth and stabilization of mesoscopic structures. *Surf. Sci. Rep.* **29**, 193-263.

Johnson, K.L. (1985) *Contact Mechanics*, Cambridge University Press, UK.

Kern, K., Niebus, H., Schatz, A., Zeppenfeld, P., George, J., Comsa, G. (1991) Long-range spatial self-organization in the adsorbate-induced restructuring of surfaces: Cu{110}-(2x1) O. *Phys. Rev. Lett.* **67**, 855-858.

Khachaturyan, A.G. (1983) *Theory of Structural Transformation in Solids*, Wiley, New York.

Li, D., Diercks, V., Pearson, J., Jiang, J.S., and Bader, S.D. (1999) Structural and magnetic studies of fcc Fe films with self-organized lateral modulation on striped Cu{110}-O(2x1) substrates. *J. Appl. Phys.* **85**, 5285-5287.

Lu, W. and Suo, Z. (1999) Coarsening, refining, and pattern emergence in binary epilayers, the Fred Lange Festschrift in the journal *Zeitschrift fur Metallkunde*. In Press.

McMeeking, R.M. and Kuhn, L.T. (1992) A diffusional creep law for powder compacts. *Acta Metall. Mater.* **40**, 961-969**.**

Mullins, W.W. (1957) Theory of thermal grooving, *J. Appl. Phys*., **28**, 333-339.

Needleman, A and Rice, J.R. (1980) Plastic creep flow effects in the diffusive cavitation of grain boundaries. *Acta Metall.* **28**, 1315-1332.

Ng, K.-O. and Vanderbilt, D. (1995) Stability of periodic domain structures in a two dimensional dipolar model. *Phys. Rev.* B **52**, 2177-2183.

Pohl, K., Bartelt, M.C., de la Figuera, J., Bartelt, N.C., Hrbek, J., Hwang, R.Q. (1999) Identifying the forces responsible for self-organization of nanostructures at crystal surfaces. *Nature* **397**, 238-241.

Pompe, W., Gong, X., Suo, Z. and Speck, J.S. (1993) Elastic energy release due to domain formation in the strained epitaxy of ferroelectric and ferroelastic films. *J. Appl. Phys*. **74**, 6012-6019.

Prigogine, I. (1967) *Introduction of Thermodynamics of Irreversible Processes*, 3rd edition, Wiley, New York.

Rayleigh, J.W.S. (1894) *The Theory of Sound*, Vol. 1, Art. 81. Reprinted by Dover, New York.

Rice, J.R. and Chuang, T.-J. (1981) Energy variations in diffusive cavity growth. *J. Am. Ceram. Soc*. **64**, 46-53.

Roytburd, A.L. (1993) Elastic domians and polydomain phases in solids. *Phase Transitions*, **45**, 1-33.

Srolovitz, D.J. (1989) On the stability of surfaces of stressed solids. *Acta Metall.* **37**, 621-625.

Suo, Z. (1997) Motions of microscopic surfaces in materials. Advances in Applied Mechanics. **33**, 193-294.

Suo, Z. (1998) Stress and strain in ferroelectrics. *Current Opinion in Solid State & Materials Sicence*, **3**, 486-489.

Suo, Z. (2000) Evolving materials structures of small feature sizes. *Int. J. Solids Structures*. **37**, 367-378.

Suo, Z. and Lu, W. (2000) Composition modulation and nanophase separation in a binary epilayer, *J. Mech. Phys. Solids*. In press.

Willis, J.R. and Bullough, R. (1969) The interaction of finite gas bubbles in a solid. *J. Nuclear Mater*. **32**, 76-87.

Wu, C.H. (1996) The chemical potential for stress-driven surface diffusion. *J. Mech. Phys. Solids* **44**, 2059-2077.