

# Self-assembled nanostructures through wavelength-controlled spinodal decomposition

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(Received 10 December 2002; accepted 18 June 2003)

The self-assembly of nanostructured materials through controlled wavelength spinodal decomposition is explored using a simple model. The model assumes that a homogeneous alloy is deposited on a rigid, periodically strained substrate. A linear stability analysis establishes that the film will undergo spinodal decomposition with the dominant wavelength determined by the periodicity of the substrate strain. © 2003 American Institute of Physics.

[DOI: 10.1063/1.1602581]

Current magnetic recording technology is bounded by the superparamagnetic limit. To achieve maximum bit density at this limit requires the recording media to be composed of an array of 8–9 nm single domain ferromagnetic particles with a monodisperse distribution of particle sizes.<sup>1</sup> Creation of such structures using lithography is not currently economically feasible, nor is one likely to achieve the required uniformity through direct deposition methods.

It has been argued theoretically,<sup>2,3</sup> and demonstrated experimentally,<sup>4</sup> that an array of misfit dislocations may introduce a preferred length scale during submonolayer epitaxial growth. Under favorable conditions one may grow highly ordered arrays of misfit dislocations,<sup>5–7</sup> yielding a periodically strained film surface. If this strained film is now used as a substrate for the growth of a second alloy film, and this second film is unstable to spinodal decomposition, one expects intuitively that the preferred wavelength for the decomposition will be dictated by the substrate strain. Hence, such a system offers the opportunity to generate nanostructured materials that may be suitable for technological applications.

It is demonstrated here, using a linear stability analysis of a simple model, that the most unstable wavelength in the decomposing film is set by the periodicity of the substrate and that a thin film not subject to spinodal decomposition will still develop a periodicity dictated by the substrate. Further, even in the absence of a periodically strained substrate, films not unstable to spinodal decomposition in the bulk may display spinodal decomposition in a thin film, a conclusion consistent with those of Refs. 8–10.

The studied rudimentary model of spinodal decomposition is depicted in Fig. 1. An elastically isotropic binary  $A-B$  alloy is deposited on a rigid substrate (i.e., it is assumed that the film is much more compliant than the substrate) with a periodically varying lattice parameter along the  $x$  direction only. The alloy is assumed to have elastic moduli and surface energy independent of composition but the two species comprising the film differ in molar volumes.

The film is initially homogeneous, with a concentration  $C_o$  of  $B$ , such that there is no *net* lattice mismatch with the substrate. This results in the  $x$  component of the total strain of the film at the interface being  $\epsilon_{xx}^T(x, -h) = \epsilon_s \cos(\kappa_s x)$ .

The stability of the homogeneous film with respect to segregation is assessed by calculating the change in free energy of the film associated with the introduction of a concentration wave with infinitesimal amplitude. This free energy change includes two contributions: one arising from the chemical composition of the film, and another arising from elastic strains.

The analysis presented here follows closely that of Cahn,<sup>11</sup> and is similar in spirit to the prior analysis of thin-film spinodal decomposition.<sup>8,12–14</sup> The concentration is chosen to be

$$C(x, y, z) = C_o + \Delta C \cos(\kappa_c x), \quad (1)$$

with  $\Delta C \ll C_o$ . The composition fluctuation is assumed to be uniform throughout the film thickness and neglects any morphological instabilities in the film surface. This assumed structure is correct in the limit  $h \ll \kappa_c^{-1}$ . In the more general case, the assumed structure may *preclude* the most unstable mode. However, if the film is unstable with respect to the growth of this constrained composition fluctuation, then the film is certainly unstable to the growth of the lowest energy concentration fluctuation.

The mean chemical free energy density of the film is

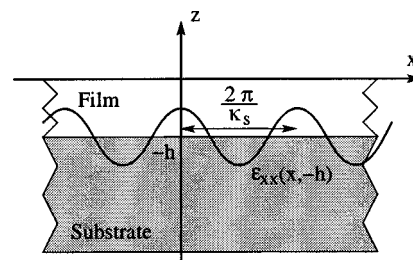


FIG. 1. Diagram showing infinite homogeneous isotropic elastic film on a rigid substrate with a periodic lattice constant. The origin is at the free surface of the film.

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$$\langle f_{\text{ch}} \rangle = f_0 + \left( \frac{f_2}{4} + \frac{\Gamma \kappa_c^2}{2} \right) \Delta C^2, \quad (2)$$

with  $f_i = (\partial^i f / \partial C^i)_{C=C_0}$ , and  $\Gamma$  describing the excess gradient free energy associated with the fluctuation.

The total strain tensor,  $\epsilon^T(x, z)$  in the film can be considered to have three components:  $\epsilon^T(x, z) = \epsilon^S(x, z) + \epsilon^C(x, z) + \epsilon^{\text{SF}}(x)$ . Here,  $\epsilon^S(x, z)$  is elastic strain imposed on the film by the substrate,  $\epsilon^{\text{SF}}(x)$  is the dilatational stress free strain that accompanies the change in local concentration, and  $\epsilon^C(x, z)$  is the elastic strain induced by the stress free strain so that  $\epsilon^T(x, z)$  satisfies the condition of compatibility. The present problem may then be solved by writing Hooke's law incorporating the stress free strain, and then solving the appropriate partial differential equation. This approach, while obviously correct, is not the most intuitive. Here, an alternative, more intuitive solution is presented.

The substrate imposes a condition of plane strain that is independent of the concentration fluctuation, so  $\epsilon^S(x, z)$  must independently satisfy the condition of compatibility, and thus can be found by solving the biharmonic equation,  $\nabla^4 \psi = 0$ , where  $\psi$  is the Airy stress function. This equation is simply the compatibility condition for plane stress where the strains are written in terms of the stresses (using Hooke's law) and the stresses are, in turn, written in terms of the Airy stress function (satisfying the equilibrium equation). The general form of the stress function for the current problem is

$$\psi(x, z) = \{A \sin(\kappa x) + \cos(\kappa x)\} \{(\alpha_0 + \alpha_1 z) \sinh(\kappa z) + (\beta_0 + \beta_1 z) \cosh(\kappa z)\}. \quad (3)$$

$\epsilon^S(x, z)$  is computed by finding  $A$ ,  $\alpha_0$ ,  $\alpha_1$ ,  $\beta_0$ , and  $\beta_1$ , which satisfy the boundary conditions of no surface tractions and coherence with the substrate.

The compatibility strain,  $\epsilon^C(x, z)$ , is found by considering the elastic strain tensor,  $\epsilon^B(x)$ , of a bulk solid containing a concentration plane wave (after Cahn<sup>11</sup>), and adding a corrective strain to remove surface tractions. Since both  $\epsilon^S(x, z)$ , and  $\epsilon^B(x) + \epsilon^{\text{SF}}(x)$  independently satisfy the condition of compatibility, then the corrective stress also satisfies the biharmonic equation and can be found by forcing the stress function in Eq. (3) to be coherent with a uniform substrate and cancel the surface tractions resulting from  $\epsilon^B(x)$ .

Computing the strain state in this fashion allows the elastic energy to be calculated as the sum of the elastic energy of a plane wave heterogeneity in a bulk material plus the work done as the interfacial and surface corrective strains are applied. This procedure yields an elastic energy density

$$\langle E_{\text{el}} \rangle = \langle E_{\text{bulk}} \rangle - a_{\text{cc}}(\theta_c)(1 + \nu)^2 \epsilon_c^2 + a_{\text{ss}}(\theta_s)(1 - \nu)^2 \epsilon_s^2 - \delta_{\kappa_s, \kappa_c} a_{\text{cs}}(\theta_s)(1 - \nu^2) \epsilon_c \epsilon_s, \quad (4)$$

with  $\delta_{\kappa_s, \kappa_c}$  the Kronecker delta,  $\theta_c = h \kappa_c$ ,  $\theta_s = h \kappa_s$ , and

$$\langle E_{\text{bulk}} \rangle = \mu \epsilon_c^2 \frac{1 + \nu}{1 - \nu}, \quad (5)$$

$$a_{\text{cc}}(\theta) = 8 W_o(\theta) \sinh^2(\theta/2) \{ \theta + (1 - 2\nu) \sinh(\theta) \}, \quad (6)$$

$$a_{\text{ss}}(\theta) = W_o(\theta) [2\theta + \sinh(2\theta)], \quad (7)$$

$$a_{\text{cs}}(\theta) = 4 W_o(\theta) [ \theta - \theta \cosh(\theta) + (1 - 2\nu) \sinh(\theta) ] + 2 W_o(\theta) \sinh(2\theta), \quad (8)$$

$$W_o(\theta) = \frac{\mu}{\theta(1 - \nu)} \{ 5 + 2\theta^2 - [4\nu(3 - 2\nu) + (3 - 4\nu) \cosh(2\theta)] \}^{-1}. \quad (9)$$

Here,  $\mu$  and  $\nu$  are the shear modulus and Poisson's ratio of the film, and  $\epsilon_c = \Delta V \Delta C / 3$ , with  $\Delta V = V_B - V_A$ , where  $V_A$  and  $V_B$  are the molar volumes of the pure components. In the limit that the film is very thin in comparison to the heterogeneity and interface strain periods ( $\theta \rightarrow 0$ ), the mean elastic energy density becomes

$$\langle E_{\text{el}} \rangle \rightarrow \frac{\mu}{1 - \nu} \left\{ \epsilon_c^2 (1 + \nu) + \frac{\epsilon_s^2}{2} - \delta_{\kappa_s, \kappa_c} \epsilon_c \epsilon_s (1 + \nu) \right\}. \quad (10)$$

In the limit of the thick film the elastic energy becomes that of the infinite solid in Eq. (5).

An infinitesimal fluctuation will grow if the mean free energy density of the system ( $\langle E_{\text{el}} \rangle + \langle f_{\text{ch}} \rangle$ ) is decreased with increasing concentration amplitude. The only contribution to the free energy is linear in  $\Delta C$ , defined to be  $\Delta f_{\text{lin}}$ , proportional to  $\delta_{\kappa_s, \kappa_c}$ , and is given by

$$\Delta f_{\text{lin}} = -a_{\text{cs}}(\theta_s)(1 - \nu^2) \epsilon_s \frac{\Delta V \Delta C}{3}. \quad (11)$$

The function  $a_{\text{cs}}(\theta)$  is positive for all  $\theta$ , so the film is unstable with respect to the growth of a composition fluctuation that matches the substrate strain. Since the reduction in free energy due to this term is linear in  $\Delta C$ , this mode is the most unstable during the initial stages of decomposition. Furthermore, the instability of the film to first order in  $\Delta C$  is dictated *entirely* by the elastic properties of the film: chemical contributions to the free energy do not affect this instability. Therefore, this instability occurs in all alloy films with  $\Delta V \neq 0$  on a strained substrate *regardless of whether the bulk system displays a miscibility gap*. Further, this instability can appear at technologically relevant wavelengths smaller than those accessible to chemically driven spinodal decomposition.

At all other wavelengths, the stability of the film to concentration fluctuations is determined by terms of order  $\Delta C^2$ . These terms are defined as  $\Delta f_{\text{quad}}$  and are

$$\Delta f_{\text{quad}} = \left\{ \frac{q(\kappa_c)}{4} - a_{\text{cc}}(\theta_c)(1 + \nu)^2 \frac{\Delta V^2}{9} \right\} \Delta C^2, \quad (12)$$

with

$$q(\kappa_c) = f_2 + 2\Gamma \kappa_c^2 + 4\mu \frac{\Delta V^2 (1 + \nu)}{9(1 - \nu)}. \quad (13)$$

The film is unstable with respect to the growth of composition waves with wave vector  $\kappa_c$  if the term in braces in Eq. (12) is negative, while the stability of bulk modes depends on the sign of  $q(\kappa_c)$ . The function  $a_{\text{cc}}(\theta)$  is zero in the limits that  $\theta \rightarrow \infty$  and  $\theta \rightarrow 0$  (the bulk solid and the infinitesimal film) and positive everywhere in between. It can be seen from Eq. (12) that alloys that as bulk solids are strain stabilized may be unstable when in the form of a film. Moreover, Downloaded 15 Jun 2005 to 128.32.120.48. Redistribution subject to AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

in such cases, the  $\kappa_c=0$  mode will not be the first to go unstable (as is the case for bulk alloys), but there will be a closed domain of unstable modes with a length scale governed by the film thickness.

Simply knowing that an alloy film will segregate is not sufficient for deciding if an alloy is a suitable candidate for producing self-assembled nanostructures. It is necessary also to understand the extent of segregation, and the relative amplification rates of competing modes. The driving force for evolution of a composition fluctuation is the variation in the mean total free energy,  $\langle \delta f_{\text{tot}} \rangle$ , which accompanies a variation in the concentration,  $\delta C(\mathbf{r})$ . Following Cahn, the general form of this variation is

$$\langle \delta f_{\text{tot}} \rangle = \int_{V'} \frac{1}{V} \left[ f_1 + f_2 \tilde{C} - 2\Gamma \nabla^2 \tilde{C} + \frac{\delta E_{\text{el}}}{\delta C} \right] \delta C dV, \quad (14)$$

where the composition distribution is given by  $C(\mathbf{r}) = C_0 + \tilde{C}(\mathbf{r})$ . The term in brackets in Eq. (14) is the chemical potential,  $\eta(\mathbf{r})$ , so if evolution of the composition distribution is diffusion mediated then the change in concentration with time is given by  $\partial \tilde{C} / \partial t = \nabla [M \nabla \eta(\mathbf{r})]$  where  $M$  is a mobility coefficient. This diffusion equation must be solved such that the change in concentration with time is consistent with the  $\delta C(\mathbf{r})$  for which  $\eta(\mathbf{r})$  is calculated. In general, the assumed form for the heterogeneity [Eq. (1)] does not satisfy this requirement, and one cannot predict the amplification rate of the unstable modes presented above.

In the limit that the film is very thin the elastic energy Eq. (10) tends to be that of a film in which there is no  $z$  component of the strain. In this limit the assumed form of the composition fluctuation becomes meaningful. Solving the diffusion equation at this limit gives

$$\begin{aligned} \tilde{C}(t, x) = & \frac{p \cos(\kappa_s x)}{q(\kappa_s)} (1 - e^{-M \kappa_s^2 q(\kappa_s) t}) \\ & + \int_{-\infty}^{\infty} d\kappa \phi_{\kappa} e^{i\kappa x} e^{-M \kappa^2 q(\kappa) t}, \end{aligned} \quad (15)$$

where  $p = \epsilon_s \mu (2\Delta V/3) [(1+\nu)/(1-\nu)]$  and  $\phi_{\kappa}$  is the  $\kappa$ th Fourier component of the initial concentration distribution. As is the case with a bulk solid, *all* fluctuations with  $q(\kappa) < 0$  will grow exponentially until the assumed linearity is no longer valid. Fluctuations with  $q(\kappa) > 0$  will decay to zero with the exception of the fluctuation in phase with the substrate strain which approach a steady state composition profile:

$$\tilde{C}(\infty, x) = \frac{P}{q(\kappa_s)} \cos(\kappa_s x). \quad (16)$$

An estimate of the amplitude of this fluctuation for a material in which bulk spinodal decomposition is inhibited by the elastic strain indicates that the steady state amplitude of this concentration wave can be large enough to invalidate the linear assumptions made here, so the effect is expected to be significant.<sup>14</sup>

In conclusion, it is demonstrated that alloy films deposited on a periodically strained substrate may spinodally decompose and the initially most unstable concentration fluctuation uniform throughout the thickness of the film has a wavelength determined by the periodicity of the substrate. While there may be concentration fluctuations more unstable than those considered here, the current calculation establishes rigorously the instability of some thin films to spinodal decomposition at the nanometer scale. In the thin film limit, the assumed form of the composition fluctuations is the expected form, and the linear amplification rates can be obtained. Hence, wavelength-controlled spinodal decomposition is a viable candidate for the self-organized growth of nanostructures.

This work is supported by the National Science Foundation, under Grant No. EEC-0085569. The authors thank Advanced Micro Devices for their generous contribution of hardware, and Lawrence Berkeley National Laboratories for providing additional computational resources.

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<sup>13</sup>A similar analysis was applied by Léonard and Desai, their work, however, studied decomposition during growth and mediated by surface diffusion only (see Ref. 3).

<sup>14</sup>Values for  $\Gamma$  and  $f_2$  were estimated for a typical immiscible fcc metal alloy by bond counting arguments following Khachaturyan (see Ref. 12).