

On the Manipulation of Nanoscale Self-Assembly by Elastic Field

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ABSTRACT

Morphological and compositional self-assembly can be manipulated by the long-range elastic field. This paper gives a universal formulation that determines the dependence of energetically favored orientation of those self-assembled structures on the elastic interaction. Elasticity anisotropy can lead to symmetry breaking and herringbone structures. A layered substrate can tune the feature size by modulus mismatch, or tune the orientation if the layers have different orientation preference, or guide the self-assembly by embedded structures. A closed-form result is derived for elastically isotropic layers by using Dundurs parameters. The self-assembled structures can also be affected by a nonuniform residual stress field or external force field. Higher order (nonlinear) perturbation theory, coupling between morphology and composition, and other issues are also addressed in the discussion.

INTRODUCTION

Nanoscale self-assembled structures offer many opportunities in growing uniform nanostructures with long-range orders and regular sizes. Surface self-assembly is usually due to the competition of surface energy and a force field [1-6]. This paper discusses how to manipulate nanoscale self-assembly by engineering the long-range elastic field. We focus our attention to morphological and compositional self-assembly. Examples of such phenomena can be found in adsorbate-induced surface restructuring, quantum dot formation, binary epitaxial thin films, among many others.

Morphological self-assembly

Under certain conditions, the nominally flat surface of a stressed solid can be unstable, leading to morphological instability (see, for instance, [1] and references therein). The elastic energy of a stressed solid with a wavy surface is always smaller than that with a flat surface. Elastic interaction can be better accommodated for morphological modulations with large frequencies (short wavelengths), which, however, gives rise to large surface energy. The competition between elastic energy and surface energy selects a critical wavelength above which perturbations grow and below which they decay. The morphological change is effected either by materials diffusing on the surface or by directly exchanging materials with the environment (e.g., evaporation/condensation, chemical etching).

The chemical potential field along the surface is $\chi = \chi_0 + \Omega(\gamma\kappa + w)$, where χ_0 is the chemical potential field of the stress-free flat solid, Ω is the atomic volume, γ is the interface energy density, κ is the curvature (positive if the surface is convex), and w is the strain energy density on the solid surface. The mechanical equilibrium is assumed to be always attained, but

the system is not in chemical equilibrium. The morphological modulation gives rise to a nonuniform chemical potential field along the surface, which provides the driving force for diffusive mass transport or direct mass exchange with the environment.

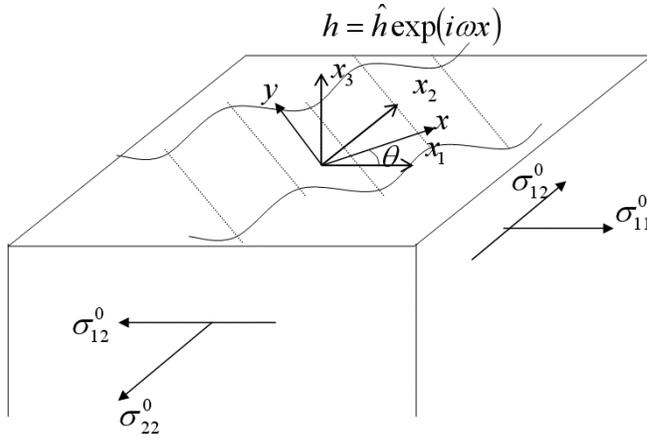


Figure 1. Schematic of a semi-infinite solid subjected to uniform remote stress fields $\sigma_{\alpha\beta}^0$ and with a single sinusoidal surface height modulation.

The elastic field due to the small morphological modulation consists of the uniform stress fields $\sigma_{\alpha\beta}^0$ and perturbation solutions. The linear perturbation solution (notations with superscript asterisk) is equivalent to that of a half-space subjected to surface tractions $\sigma_{3\alpha}^* = \sigma_{\alpha\beta}^0 h_{,\beta}$ [1]. The elasticity boundary value problem can be solved analytically in the Fourier space. Represent the surface roughness $h(x_1, x_2)$ by a two-dimensional Fourier transformation:

$$h(x_1, x_2) = \iint \hat{h}(\omega_1, \omega_2) \exp(i\omega_1 x_1 + i\omega_2 x_2) d\omega_1 d\omega_2, \quad (1)$$

where (ω_1, ω_2) is the wavevector. The elastic field in the solid depends on three spatial coordinates, but is a linear superposition of many Fourier components, each being a two-dimensional field in the plane spanned by x_3 and $\omega_\alpha x_\alpha$ (see Fig. 1). Pick up one Fourier component that varies along x direction, which makes an angle θ from x_1 direction in (x_1, x_2) plane. Let $\omega = \sqrt{\omega_1^2 + \omega_2^2}$, so that $(\omega_1, \omega_2) = \omega(\cos \theta, \sin \theta)$.

The elastic field of a semi-infinite space (which could be a laminated structure) subjected to surface sinusoidal traction is given in previous work [2]. To the first order, the elastic energy scales as

$$\Theta = \mathbf{m}^T \mathbf{B} \mathbf{m}, \quad (2)$$

where

$$\mathbf{m} = (\sigma_{11}^0 \cos \theta + \sigma_{12}^0 \sin \theta, \sigma_{12}^0 \cos \theta + \sigma_{22}^0 \sin \theta, 0)^T, \quad (3)$$

and matrix \mathbf{B} depends on the elastic constants and the orientation θ . This representation is independent of mass transport mechanism on the surface. The orientation of fastest growth frequency is determined by maximizing Eq. (2) as a function of θ with varying anisotropy in the applied stress and substrate stiffness [3].

Compositional self-assembly

Consider the surface stress-stabilized phase patterns in a binary monolayer [2, 4-6]. When the concentration modulates in an adsorbed binary monolayer on a solid surface, the surface stress becomes nonuniform, causing an elastic field inside the substrate. To better accommodate the surface stress nonuniformity, large phases will break into small phases. The total length of phase boundaries, however, increases and so does the phase boundary energy. It is the competition between the phase boundary energy and the elastic energy that stabilizes the phase patterns and selects an equilibrium phase size.

Schematic in Fig. 1 is also applicable to this problem if we replace the surface roughness $h(x_1, x_2)$ by the concentration field $C(x_1, x_2)$, and the applied stress $\sigma_{\alpha\beta}^0$ by the surface stress. The surface stress is the excess work per unit area done when the surface enlarges per unit strain, and in general is a second-rank tensor $f_{\alpha\beta}$. We assume that the surface stress is linear in the concentration C . That is, when the concentration changes by ΔC , the surface stress changes by $\Delta f_{\alpha\beta} = \phi_{\alpha\beta} \Delta C$. The slope tensor $\phi_{\alpha\beta}$ can be measured by the wafer curvature method or determined by electronic structure calculations.

The thermodynamic theory [4-6] shows that the substrate is stressed with surface traction $\sigma_{3\alpha} = \phi_{\alpha\beta} C_{,\beta}$ (at $x_3 = 0$). Similar as the procedure in the previous subsection, we solve the elasticity boundary value problem in the Fourier space. The concentration field can be represented by a two-dimensional Fourier transformation, similar as Eq. (1). Pick up one Fourier component, and the surface traction is also in a sinusoidal form. The elastic interaction also scales as Eq. (2) with $\mathbf{m} = (\phi_{11} \cos \theta + \phi_{12} \sin \theta, \phi_{12} \cos \theta + \phi_{22} \sin \theta, 0)^T$. The orientation of equilibrium compositional pattern is again determined by maximizing Eq. (2) as a function of θ with varying anisotropy in the surface stress and the substrate stiffness tensor.

We obtain the same orientation dependence function Θ for morphological and compositional self-assembly, because the elasticity boundary value problem is the same if we replace the height field by the concentration field, and regard the surface stress as the applied stress in a thin membrane. Consequently, results in [2, 5-6] can be directly applied to morphological self-assembly. The following section gives a brief summary of results.

ELASTICITY AND SYMMETRY BREAKING

The dependence of energetically favored orientation on the anisotropy is called symmetry breaking in this paper. As pointed out in previous section, same results are anticipated for the anisotropy in the applied stress tensor for the morphological self-assembly and the anisotropy in the surface stress tensor for the compositional self-assembly. Consequently, those kinds of

anisotropy will be called the anisotropy in vector \mathbf{m} . Anisotropy in stiffness tensor is called the anisotropy in matrix \mathbf{B} .

When the solid is elastically isotropic, we have shown that depending on the anisotropy in vector \mathbf{m} , the energetically favored orientation could orient along or at an angle from a principal axis of the surface stress tensor or applied stress tensor. This phenomenon has been studied in [5], and a physical interpretation is given. That is, the along-axis to off-axis transition compromises the elastic energy of the inplane and antiplane deformation, where the plane is (x, x_3) as shown in Fig. 1. If one nontrivial angle θ is selected, symmetry operation dictates that $\pi/2 - \theta$ is also possible. The coexistence of them leads to a mesoscale herringbone structure, further relaxing the elastic free energy. Similar results have also been found in the formation of herringbone structure in thin film buckling problem [7].

When vector \mathbf{m} is isotropic, elementary consideration shows that the energetically favored orientation should be the most compliant direction in tension and shear [2, 6]. For the (100) surface of a cubic crystal, the shear modulus in any (x, x_3) plane is the same. The most compliant directions in tension are the crystalline axes. Numerical simulation of strained epitaxial thin film indeed shows that quantum dots form regular arrays along $\langle 100 \rangle$ directions [8]. In general, there could be many forms of anisotropy, and one needs to evaluate function Θ to determine the preferred orientation.

LAYERED SOLID

When the solid is of a layered structure, the effect of stiffness tensors of underneath layers will be passed to the surface through the long-range elastic field. Consequently, we can tune the wavelength of morphological and compositional modulation by modulus mismatch of those layers. For example, a compliant layer inside will amplify the effect of elastic interaction and lead to smaller feature size. We can also tune the orientation if the layers have different orientation preference. However, the elastic field in a half-space subjected to a sinusoidal traction decays exponentially into the solid with a decay length proportional to the wavelength of the surface waviness or the concentration modulation. Consequently, in order to make the stiffness tensors of underlying layers effective, the thickness of the first layer must be comparable with the decay length. For example, at the early stage of epitaxial growth of thin film on a substrate, the formation of quantum dots can follow the orientation preference of the substrate.

The elasticity boundary value problem is solved in [2], and many examples of passing stiffness anisotropy in multilayer and the effect on nanoscale compositional self-assembly have been discussed there. When the substrate is of two elastically isotropic materials, we can derive a closed-form solution of matrix \mathbf{B} in Eq. (2). Suppose layer I is at the top with thickness d and layer II extends to $x_3 \rightarrow -\infty$. Matrix \mathbf{B} is then a function of elastic constants of the two layers and ωd , where ω is the frequency of a given morphological or compositional sinusoidal modulation. Define two Dundurs parameters

$$\alpha = \frac{\mu_{\text{II}}(1-\nu_{\text{I}}) - \mu_{\text{I}}(1-\nu_{\text{II}})}{\mu_{\text{II}}(1-\nu_{\text{I}}) + \mu_{\text{I}}(1-\nu_{\text{II}})}, \quad \beta = \frac{\mu_{\text{II}}(1-2\nu_{\text{I}}) - \mu_{\text{I}}(1-2\nu_{\text{II}})}{2[\mu_{\text{II}}(1-\nu_{\text{I}}) + \mu_{\text{I}}(1-\nu_{\text{II}})]}, \quad (4)$$

which are restricted in the parallelogram bounded by $\alpha = \pm 1$ and $\alpha - 4\beta = \pm 1$. The matrix \mathbf{B} is

$$\mathbf{B} = \frac{1}{\mu_1} \begin{bmatrix} (1-\nu_1)\frac{R_{11}}{R} & 0 & -i\left(\frac{1}{2}-\nu_1\right)\frac{R_{13}}{R} \\ 0 & R_{22} & 0 \\ i\left(\frac{1}{2}-\nu_1\right)\frac{R_{13}}{R} & 0 & (1-\nu_1)\frac{R_{33}}{R} \end{bmatrix}, \quad (5)$$

$$R = (1-\beta^2)\exp(4\omega d) + [4(\omega d)^2(1-\beta)(\alpha-\beta) + 2(\alpha+\beta^2)]\exp(2\omega d) + \alpha^2 - \beta^2, \quad (6)$$

$$R_{11} = (1-\beta^2)\exp(4\omega d) + 4\omega d(1-\beta)(\alpha-\beta)\exp(2\omega d) + \beta^2 - \alpha^2, \quad (7)$$

$$R_{13} = (\beta^2 - 1)\exp(4\omega d) + 4(\omega d)^2(1-\beta)(\alpha-\beta)\exp(2\omega d)/(1-2\nu_1) + 2\exp(2\omega d)[-(\alpha+\beta^2) + 2\beta(1+\alpha)(1-\nu_1)/(1-2\nu_1)] + \beta^2 - \alpha^2, \quad (8)$$

$$R_{33} = (1-\beta^2)\exp(4\omega d) - 4\omega d(1-\beta)(\alpha-\beta)\exp(2\omega d) + \beta^2 - \alpha^2. \quad (9)$$

$$R_{22} = [(\mu_{II} + \mu_I)\exp(\omega d) - (\mu_{II} - \mu_I)\exp(-\omega d)]/[(\mu_{II} + \mu_I)\exp(\omega d) + (\mu_{II} - \mu_I)\exp(-\omega d)], \quad (10)$$

If the surface stress or the applied stress is isotropic, the function Θ scales as $\frac{(1-\nu_1)R_{11}}{\mu_1 R}$.

Figure 2 plots R_{11}/R as a function of normalized thickness of layer I with several values of Dundurs parameters. Clearly, to change the magnitude of elastic interaction significantly, the thickness must be comparable with the self-assembly feature size. The method presented here gives more general results than that in Spencer et al. [9], and it can be directly used for elastically anisotropic materials (see [2] for calculations of matrix \mathbf{B} for general cases). Furthermore, using the above method, one can easily obtain the dependence of critical and fastest growth frequencies as a function of thin film thickness for morphological self-assembly with a given type of kinetics [3].

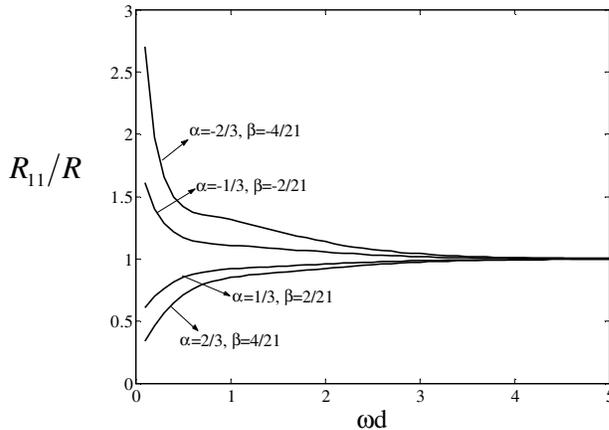


Figure 2. The magnitude of elastic interaction, R_{11}/R , as a function of the normalized thickness of the first layer ωd with several values of Dundurs parameters.

GUIDED SELF-ASSEMBLY

Using anisotropy to break the orientational symmetry is promising but might have many other practical difficulties. One more powerful method is to guide the self-assembly by an

external force field. For electrically-induced compositional self-assembly, the introduction of external charge field can successfully guide the concentration field [10]. Let us consider the morphological self-assembly discussed in this paper. If there is an external force field (notations with superscript “ext”), by the elasticity reciprocal theorem, the strain energy density at the surface changes by $\Delta w = -\sigma_{\alpha\beta}^0 h_{,\beta} u_{\alpha}^{ext}$. The external field will affect the natural frequency spectrum of the self-assembly [3]. An external field can be obtained by introducing defects such as dislocations, or residual stress field.

DISCUSSIONS

Nanoscale self-assembly on solid surfaces has offered many opportunities in nanostructure fabrications, e.g., as templates for making devices. We consider morphological and compositional self-assembly and investigate how to manipulate those self-organized structures by the elastic field. A quadratic form, Eq. (1), is derived to determine the energetically favored orientation with varying anisotropy in stiffness and applied stress or surface stress. This representation is the same for morphological and compositional self-assembly to the first order of perturbation. Consequently, if an epitaxial thin film has both morphology and composition modulation and the coupling contains only higher order term, we expect no difference from individual self-assembly [11].

Generally, higher order perturbation solution will give us different orientation preference [3]. However, this is hardly observed in experiments because the magnitude of nonlinear interaction is usually small compared with the linear interaction. Currently, we are trying to apply the higher order perturbation solution to a fractal rough-surface subjected to stress and surface reaction [3]. The higher order perturbation allows us to couple the scales and explore the size effect. The effect of higher order perturbation is also pronounced near surface defect [12].

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