

# 行政院國家科學委員會補助專題研究計畫成果報告

## 合金薄膜形態變化之穩定分析

### Morphological Stability of Alloy Thin Films

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#### 中文摘要

本研究計劃乃探討半導體合金薄膜型態變化之穩定分析；此項研究在加強與擴展半導體領域上是極具有發展潛力的。我們藉由發展材料多重尺度模型，來建構本研究之理論基礎，並提出一種全新的構想，即藉由探討非均質組成濃度和薄膜表面粗糙所造成的耦合效應，來研究合金薄膜型態變化之穩定分析。同時結果顯示對合金薄膜生成中其奇異溫度的大小，乃是藉由不穩定因素諸如彈性應變能，與穩定因素諸如化學能和表面張力，之間的競爭而得到。

# NSC PROGRESS REPORT

## Morphological Stability of Alloy Thin Films

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### Abstract

We have studied the morphological stability of semiconductor alloy films with potential to enhance and enlarge the current spectrum of applications that are of interest to the semiconductor industry. We have developed a framework based on the multiscale modeling to perform stability analysis of alloy film growth accounting for the joint effect of nonuniform composition and surface roughness. We have shown that the critical temperature is obtained by the competition between the destabilizing influence of elastic strain energy and the stabilizing influence of chemical and surface energies.

### 1 Introduction

The interest in the morphology and spinodal decomposition of an alloy film has motivated many efforts to study strain relaxation by surface roughness and composition variation. It is well known that relaxation of elastic energy can have a strong influence on the morphology of a stressed solid. Recent experiment has observed a 3D morphology for a strained epitaxial film instead of common layer-by-layer growth. One possible explanation for this change of growth mode is that a stressed film can partially relieve its elastic energy by a morphological instability at the free

surface through mass transport, which gives the formation of islands, nonplanar surfaces or cusplike morphologies. Instability of this type arises as the strain energy reduction due to morphological variations in surface shape surpasses the increase of surface energy.

Strain relaxation via composition modulation is also of particular importance in the theory of spinodal decomposition. A homogeneous alloy which is not completely miscible tends to decompose under certain critical temperature [1]. Cahn was the first to demonstrate that a bulk alloy can be stabilized by the presence of coherent composition fluctuations provided the volume of its unit cell changes with composition. In the case of thin alloy films, the presence of free surface in an uncapped thin film allows the partial relaxation of coherent strain. As a result, the increase of elastic energy in a thin film turns out to be smaller than that in its bulk form for the same compositional strain modulation. The predicted critical temperature  $T_c^f$  in thin films is therefore higher than  $T_c^B$  in bulk alloys. Experimental evidence for strain relaxation via composition fluctuations and for strain-driven spinodal decomposition can be found in [5].

We study strain relief by surface roughness and composition fluctuation in a stressed alloy film here. We propose to investigate it by deriving a relaxation formula using energy bounds. We first develop suit-

able upper and lower bounds of energy, and then prove the identity of these two bounds if both film surface and compositional strain are smooth. However, if the surface profile does not have continuous derivatives as happened often in the shape transition in the growth of strained islands [7], the resulting relaxation formula turns out to be an upper bound of the strain energy.

Another advantage of the current approach is that we do not require any *a priori* assumption of elastic isotropy or identical material properties between film and substrate in deriving our results. Such a generalization is important as material inhomogeneity has great influence on the morphology of heteroepitaxially growing films. Freund and Jonsdottir [2] have demonstrated that the stability criterion is sensitive to the ratio of film thickness to roughness if both film and substrate have dissimilar material properties.

## 2 The Free Energy of an Inhomogeneous Alloy Film

### 2.1 General Problem

Consider a film/substrate system shown in Figure 1. The film surface is described by  $x_3 = \bar{h}(\mathbf{x}_p) > 0$ . Let  $S$  be the bounded Lipschitz domain,  $h$  be viewed as the average thickness of the film and  $H$  be the height of the substrate. The reference domain of the film/substrate system is denoted by

$$\Omega^{(h)} = S \times (-H, \bar{h}(\mathbf{x}_p)). \quad (2.1)$$

Set

$$\Omega_f^{(h)} = S \times (0, \bar{h}(\mathbf{x}_p)), \quad \Omega_s = S \times (-H, 0) \quad (2.2)$$

which are the domains for the film and substrate, respectively.

The total energy of the film/substrate system

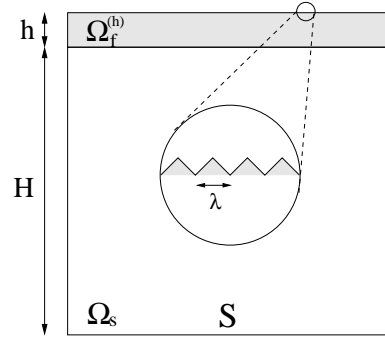


Figure 1: A heterogeneous film/substrate system with a non-flat surface.

per unit area includes

$$W_{tot}^{(h)} = W_e^{(h)} + W_s^{(h)} + W_c^{(h)}, \quad (2.3)$$

where  $W_e^{(h)}$  is the elastic energy of the film/substrate system,  $W_s^{(h)}$  the surface energy of the film surface, and  $W_c^{(h)}$  the chemical energy. The elastic energy per unit area is given by

$$W_e^{(h)} = \inf_{\mathbf{u} \in V} \frac{1}{|S|} \int_{\Omega^{(h)}} \varphi_e(\mathbf{E}[\mathbf{u}], \mathbf{x}) d\mathbf{x}, \quad (2.4)$$

where  $\varphi_e : \mathbb{M}_s^{3 \times 3} \times \mathbb{R}^3 \rightarrow [0, \infty)$  is the elastic energy density,  $\mathbf{E} \in \mathbb{M}_s^{3 \times 3}$  the strain depending on displacement  $\mathbf{u} : \Omega^{(h)} \rightarrow \mathbb{R}^3$

$$\mathbf{E}[\mathbf{u}] = \frac{1}{2} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T), \quad (2.5)$$

and the space  $V$  defined by

$$V = \left\{ \mathbf{u} : \mathbf{u} \in W^{1,2}(\Omega^{(h)}, \mathbb{R}^3), \mathbf{u}|_{S \times \{-H\}} = \mathbf{0} \right\}. \quad (2.6)$$

Note that the inhomogeneity of the film due to various causes can be seen from the dependence of  $\varphi_e$  on  $\mathbf{x}$ .

The surface energy per unit area is

$$W_s^{(h)} = \frac{1}{|S|} \int_S \gamma(\mathbf{n}) dS(\mathbf{n}), \quad (2.7)$$

where  $\gamma(\mathbf{n})$  is the surface tension depending on the film surface normal  $\mathbf{n}$ . If  $\gamma(\mathbf{n})$  is independent of orientation  $\mathbf{n}$  and is equal to  $\gamma$ , (2.7) becomes

$$W_s^{(h)} = \frac{1}{|S|} \int_S \gamma \sqrt{1 + \bar{h}_{,1}^2 + \bar{h}_{,2}^2} d\mathbf{x}_p. \quad (2.8)$$

The chemical energy per unit area is

$$W_c^{(h)} = \frac{1}{|S|} \int_{\Omega_f^{(h)}} \varphi_c(\bar{c}(\mathbf{x}_p)) d\mathbf{x}, \quad (2.9)$$

where  $\bar{c}(\mathbf{x}_p) : S \rightarrow (0, 1)$  is the concentration of the alloy film and  $\varphi_c : (0, 1) \rightarrow \mathbb{R}$  is the volume density of the chemical and entropic part of the free energy in the film. Using the regular solution model gives

$$\varphi_c(\bar{c}) = \Xi \bar{c}(1 - \bar{c}) + RT [\bar{c} \ln \bar{c} + (1 - \bar{c}) \ln (1 - \bar{c})] \quad (2.10)$$

where  $\Xi$  is the interaction parameter,  $R$  the gas constant, and  $T$  the temperature.

Consider a homogeneous alloy film with planar free surface and denote it as the reference state. We wish to study the thermodynamic instability of the alloy film by examining if any joint composition modulation  $\bar{c}(\mathbf{x})$  and surface undulation  $\bar{h}(\mathbf{x}_p)$  may lower the free energy of the reference state. Note that once the perturbed  $\bar{c}(\mathbf{x})$  and  $\bar{h}(\mathbf{x}_p)$  are given, the energies  $W_c^{(h)}$  and  $W_s^{(h)}$  can be calculated immediately by integrating (2.8) and (2.9). However, the elastic energy  $W_e^{(h)}$  is still unavailable as we need to solve the minimization problem (2.4) which is difficult in general. The analysis can be greatly simplified by assuming the periodicity of the film surface and composition and will be considered next.

### 3 Asymptotical Formulation of Limiting Elastic Energy

We now study an important case for slightly undulating surface and fluctuating composition; i.e.,  $h \ll \lambda, d$ . Instead of solving a difficult minimizing problem, we show that the asymptotical expansion of the elastic energy  $\bar{W}_e$  up to the first order in  $\alpha$  is given by the following theorem.

**Theorem 1** *Let the effective elastic energy density and eigenstress be given by  $\bar{W}_e$  and  $\sigma^{*p}$ .*

(a). *Assume*

$$\begin{aligned} \sigma^{*p}(\mathbf{x}_p) &\in W_{\text{per}}^{1,\infty}(X, \mathbb{M}_s^{2 \times 2}) \cap W_{\text{per}}^{2,2}(X, \mathbb{M}_s^{2 \times 2}), \\ f(\mathbf{x}_p) &\in W_{\text{per}}^{1,\infty}(X, \mathbb{R}) \cap W_{\text{per}}^{2,2}(X, \mathbb{R}). \end{aligned}$$

*Then,*

$$\liminf_{\alpha \rightarrow 0} \left[ \frac{1}{\alpha} (\bar{W}_e - W_0) \right] \geq W_1 + W_2, \quad (3.1)$$

*where*

$$\begin{aligned} W_0 &= \int_X U_0(\mathbf{x}_p) f(\mathbf{x}_p) d\mathbf{x}_p, \\ W_1 &= -\frac{1}{2} \int_Z \nabla_p \cdot [\sigma^{*p} f(\mathbf{x}_p)] \cdot \mathbf{u}_p^{(\infty)} d\mathbf{x}_p, \quad (3.2) \\ W_2 &= -\int_X \nabla_p \cdot [\sigma^{*p} f^2(\mathbf{x}_p)] \cdot \mathbf{b}^{*p}(\mathbf{x}_p) d\mathbf{x}_p. \end{aligned}$$

(b). *Suppose*

$$f(\mathbf{x}_p) \in W_{\text{per}}^{1,\infty}(X, \mathbb{R}), \quad \mathbf{b}^*(\mathbf{x}_p), \sigma^{*p}(\mathbf{x}_p) \in W_{\text{per}}^{1,2}(X, \mathbb{R}^3).$$

*We have*

$$\limsup_{\alpha \rightarrow 0} \left[ \frac{1}{\alpha} (\bar{W}_e - W_0) \right] \leq W_1 + W_2, \quad (3.3)$$

*where  $W_0, W_1$  and  $W_2$  are given by (3.2).*

Above, the details of notations such as  $f, U_0, \mathbf{b}^*, \mathbf{u}^{(\infty)}$  and  $\mathbf{t}$  are described in [6].

**Remark 1** If both film surface  $f(\mathbf{x}_p)$  and eigenstrain  $\mathbf{E}^I(\mathbf{x}_p)$  are smooth, Theorem 1 tells us that the limiting elastic energy of a film/substrate system can be approximated as the sum of three energies  $W_0, W_1$  and  $W_2$  provided the ratio of the film thickness to the periods of roughness and composition variation is small; i.e.,

$$\bar{W}_e = W_0 + \alpha(W_1 + W_2) + o(\alpha),$$

where  $\frac{o(\alpha)}{\alpha} \rightarrow 0$  as  $\alpha \rightarrow 0$ . On the other hand, if the surface profile does not have continuous derivatives as happened often in the shape transition in the growth of strained islands [7], the resulting relaxation formula turns out to be an upper bound of the strain energy (3.3).

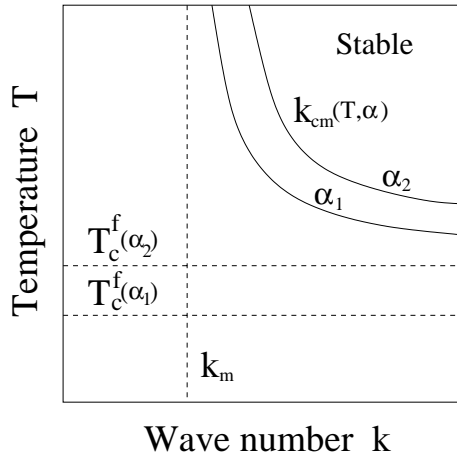


Figure 2: Instability with respect to coupled compositional and morphological modulations in a stressed alloy film deposited on a thick substrate. Here  $0 < \alpha_1 < \alpha_2$  and  $k = k_{cm}(T, \alpha)$  separates the boundary of instability in the  $k$ - $T$  plane. Dashed lines are the boundaries of independent compositional and morphological instabilities.

## 4 Stability with Respect to Morphology and Spinodal Decomposition

We now apply Theorem 1 to studying the thermodynamical stability of a nonhydrostatically stressed thin film. Suppose the film is made of a binary cubic alloy of the form  $A_{\bar{c}}B_{1-\bar{c}}$  or ternary cubic alloy of the form  $A_{\bar{c}}B_{1-\bar{c}}C$ , and its stress free lattice parameter  $a(\bar{c})$  depending on composition  $\bar{c}$  follows Vegard's law; i.e.,

$$\eta = \frac{1}{a} \frac{da}{d\bar{c}} \Big|_{c_1} \neq 0, \quad (4.1)$$

where  $\eta$  is the solute expansion coefficient.

As any smooth periodic function can be expanded by multi-dimensional Fourier series, we may assume that the compositional and morphological modulations  $\hat{h}(\mathbf{x}_p)$  and  $\hat{c}(\mathbf{x}_p)$  take all possible combinations of  $\sin(2\pi m x_1) \sin(2\pi n x_2)$ ,  $\sin(2\pi m x_1) \cos(2\pi n x_2)$ ,  $\cos(2\pi m x_1) \sin(2\pi n x_2)$ , and  $\cos(2\pi m x_1) \cos(2\pi n x_2)$ , and sum all these combinations weighting by their Fourier coefficients.

As an example, we assume that

$$\hat{h}(\mathbf{x}_p) = \sin(2\pi x_1) \sin(2\pi x_2) \quad (4.2)$$

$$\hat{c}(\mathbf{x}_p) = \sin(2\pi x_1) \sin(2\pi x_2), \quad (4.3)$$

for simplicity. We have shown that the new critical wave number separating the boundary of instability in the  $k$ - $T$  plane is

$$k_{cm}(T, \alpha) = k_m + \alpha \frac{8\pi\eta^2}{\gamma} \frac{c_1(1-c_1)}{R(T-T_c^f(\alpha))} (1+\nu)^2 \left( \frac{E}{1-\nu} \right)^2,$$

where

$$k_m = \frac{\sqrt{2}}{\gamma} (1+\nu) \frac{E}{1-\nu} e^{m^2}.$$

The result can also be shown in Figure 2. The 3D critical wave number  $k_m$  coincides with that in [3]. On the other hand, for a pure compositional modulation, there is a slight difference between the critical temperature  $T_c^f$  and that obtained by [4] in the case of small  $\alpha$ . This is because compositional modulation used here is 2D instead of 1D in [4].

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