

## Self-organized growth of composition-modulated alloys

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Epitaxial growth of semiconductor alloys in open systems can be unstable against fluctuations of composition [1-4]. For such kinetic instability it is typical that the bulk diffusion is negligibly slow compared with the surface diffusion. Fluctuations of composition in the entire thickness of the epitaxial film are “frozen”, and these fluctuations create a strain field on the surface which affects the surface migration of atoms. It was shown in [4], that due to the interplay of anisotropic elasticity and anisotropic surface diffusion, the wave vector of the most unstable mode of composition fluctuations can have any direction. However, an important question was still unsolved: How does this interplay depend on key experimental parameters, namely on growth temperature and growth velocity? Moreover, the linear stability analysis of alloy growth [1–4] does not give an answer on the final composition-modulated structure which is being formed during the growth.

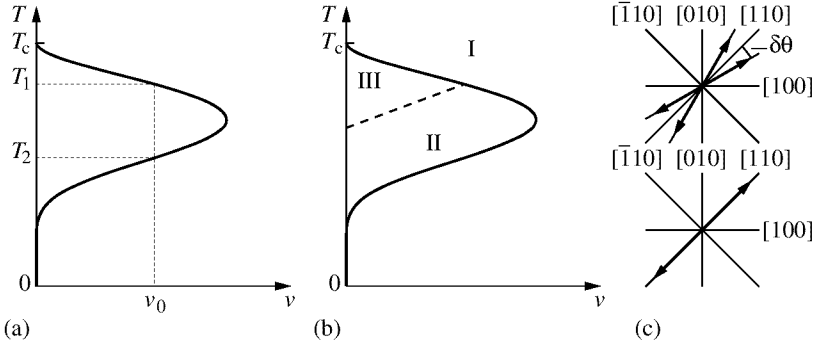
In the present paper we, first, perform a linear stability analysis and obtain the wave vector of the most unstable mode as a function of growth temperature and growth velocity. Second, we solve a non-linear problem in the weak segregation regime and obtain a final composition-modulated structure.

We study the growth of a binary alloy  $A_{1-c}B_c$  via molecular beam epitaxy at growth temperature above the roughening transition temperature. Then the surface contains a high concentration of steps and kinks. Crystal growth can be described by the propagation of the surface in the normal direction. The growth of an alloy implies coupled fluctuations of alloy composition  $\phi(\mathbf{r}_{\parallel}, z) = c(\mathbf{r}_{\parallel}, z) - \bar{c}$  and surface profile  $\zeta(\mathbf{r}_{\parallel}) = h(\mathbf{r}_{\parallel}) - \bar{h}$ , where  $h(\mathbf{r}_{\parallel})$  is the local thickness of the film, and  $\bar{h}$  is the average thickness. Let the alloy  $A_{1-c}B_c$  be a mixture of two cubic crystals, the homogeneous alloy be lattice-matched to the substrate and the growth occur on the (001)-substrate of a cubic material. The growth of an alloy is described by two coupled kinetic equations. Let the reference frame travel together with the surface with the average growth velocity  $v$ . Then kinetic equations are as follows:

$$\begin{aligned} \frac{\partial \phi(\mathbf{r}_{\parallel})}{\partial t} &= M_{ij}^{\phi} \nabla_i \nabla_j \frac{\delta F}{\delta \phi(\mathbf{r}_{\parallel}, \bar{h})} - \frac{v}{a} \phi(\mathbf{r}_{\parallel}, \bar{h}) \\ \frac{\partial \zeta(\mathbf{r}_{\parallel})}{\partial t} &= M_{ij}^{\zeta} \nabla_i \nabla_j \frac{\delta F}{\delta \zeta(\mathbf{r}_{\parallel})}. \end{aligned} \quad (1)$$

Here  $M_{ij}^{\phi}$  and  $M_{ij}^{\zeta}$  are 2D surface atomic mobility tensors related to the substitutional diffusion and to the change of surface profile, respectively. Unlike [3], Eqs.(1) account the anisotropy of surface mobility tensors, their principle axes being  $[110]$  and  $[\bar{1}10]$ , which is typical for III-V and II-VI semiconductors;  $a$  is the lattice parameter. The free energy  $F$  equals  $F_{chem} + F_{grad} + E_{surf} + E_{el}$ , where  $F_{chem}$  is the chemical free energy,  $F_{grad}$  is the gradient energy,  $E_{surf}$  is the surface energy of a corrugated surface, and  $E_{el}$  is the elastic energy depending on the surface profile.

First, we carry out the linear stability analysis by expanding  $F$  up to  $\phi^2$  and  $\zeta^2$ . We seek Fourier components of fluctuations  $\tilde{\phi}(\mathbf{k}_{\parallel}, t)$  and  $\tilde{\zeta}(\mathbf{k}_{\parallel}, t)$  proportional to  $\exp[\omega(\mathbf{k}_{\parallel})t]$ .



**Fig. 1.** The phase diagram of kinetic instability in variables “temperature-growth velocity”. (a) The boundary of the instability region. For  $v = v_0$  the alloy is unstable at  $T_2 < T < T_1$ . (b) I: stable alloys, II: unstable alloys, most unstable modes are shown in Fig. 1(c) (bottom). III: unstable alloys, most unstable modes are shown in Fig. 1(c) (top). (c) Wave vectors of most unstable modes.

Linearized equations for  $\tilde{\phi}(\mathbf{k}_{\parallel}, t)$  and  $\tilde{\zeta}(\mathbf{k}_{\parallel}, t)$  are decoupled, similar to [2,3]. For fluctuations of composition,  $\tilde{\phi}(\mathbf{k}_{\parallel}, t) \sim \exp[\omega(\mathbf{k}_{\parallel})t]$ , we obtain the following characteristic equation for  $\omega$ :

$$\omega = -M(\theta)k^2 \left[ r(T - T_c) + \kappa k^2 + \sum_{s=1}^3 \left( \frac{k R_s(\theta)}{k \alpha_s(\theta) + \omega/v} - \frac{R_s(0)}{\alpha_s(0)} \right) \right] - v/a. \quad (2)$$

$\theta$  is the angle between  $\mathbf{k}_{\parallel}$  and  $[100]$ ;  $R_s(\theta)$  refer to the anisotropic elastic interaction [1];  $\alpha_s(\theta)$  are attenuation coefficients of static Rayleigh waves;  $M(\theta)$  is the effective mobility in the given direction,  $M(\theta) = M_1^{\phi} \cos^2(\theta - \pi/4) + M_2^{\phi} \sin^2(\theta - \pi/4)$ , where  $M_1^{\phi}$  and  $M_2^{\phi}$  are mobilities along  $[110]$  and  $[\bar{1}10]$ ,  $T_c$  is the critical temperature of kinetic instability in the slow deposition limit ( $v \rightarrow 0$ ) [1];  $r = (\partial^3 f_{chem} / \partial c^2 \partial T)$ , where  $f_{chem}$  is the chemical free energy density;  $\kappa$  refers to the gradient energy. Given  $v$  and  $T$ , Eq.(2) determines  $\omega(k, \theta)$ .  $\text{Re} \omega > 0$  means the kinetic instability.

To obtain the stability phase diagram of the alloy growth (Fig. 1(b)) we set  $\bar{c} = 0.5$ , use for  $f_{chem}$  the regular solution approximation,  $f_{chem}(c, T) = \Omega c(1 - c) + T[(1 - c) \ln(1 - c) + c \ln c]$ , and take into account the Arrhenius-type temperature dependence of mobilities  $M_{1,2}(T) = M_{1,2}^{(0)} \exp(-E_{1,2}/T)$ . The growth of an alloy includes the competition between the surface migration and the burial by the incoming flux. Let temperature  $T$  be fixed. Then, if the growth velocity  $v$  is larger than a certain critical value, the fast burial does not allow the surface migration to create composition fluctuations. Now, let  $v$  be fixed and  $T$  decrease. When  $T < T_1(v)$ , the driving force to kinetic instability appears. When  $T < T_2(v)$  the slow surface diffusion does not allow composition fluctuations to occur (Fig. 1(a)).

Anisotropic surface diffusion promotes instability with  $\mathbf{k}_{\parallel}$  along the direction of fast diffusion  $[110]$ . Anisotropic elasticity promotes instability with  $\mathbf{k}_{\parallel}$  along the elastically soft direction  $[100]$  or  $[010]$ . The result of such an interplay is given in Fig. 1(b). In region II there are 2 most unstable modes with  $\mathbf{k}_{\parallel} \parallel [110]$ . In region III there are 4 most unstable modes with  $\mathbf{k}_{\parallel}$  deviated by  $\pm \delta\theta$  from  $[110]$  (Fig. 1(c)).

Below we seek steady state solutions in the weak segregation regime, i.e. at  $T$  and  $v$  close to the onset of the instability. For simplicity we consider isotropic surface diffusion. Near the onset of instability we have  $(v\kappa)/[aMr(T_c - T)] = 1/4 - \epsilon^2$ , where  $\epsilon \ll 1$ . The fact that in the linear regime, kinetic equations for  $\phi$  and for  $\zeta$  are decoupled and the

surface remains flat, has two important issues. First,  $\zeta \sim \phi^2$ . Then, to solve the non-linear problem we expand the free energy up to fourth order terms, i.e. up to  $\phi^4$  and  $\zeta^2$ . Second, the relaxation of the surface is a fast process, while the relaxation of the composition profile is a slow process. By using the adiabatic elimination of fast relaxing variables [5] we obtain kinetic equations which contain only  $\phi$ . In the weak segregation regime the solution is a perturbation series in  $\epsilon$ . The main contribution is given by most unstable modes with  $\mathbf{k}_{\parallel} = \pm(k_0, 0)$  and  $\mathbf{k}_{\parallel} = \pm(0, k_0)$ , where  $k_0 = (1/\sqrt{2})[r(T_c - T)/\kappa]^{1/2}$ . We seek  $\phi$  in the form  $\phi(x, y) = \epsilon[(r_4/r(T_c - T))^{1/2}[\psi_x \cos(k_0 x) + \psi_y \cos(k_0 y)]]$ , where  $r_4 = (\partial^4 f_{chem}/\partial c^4)_{c=\bar{c}}$ . Kinetic equations for amplitudes  $\psi_x$  and  $\psi_y$  are

$$\begin{aligned}\frac{\partial \psi_x}{\partial \tau} &= -\frac{\epsilon^2}{2} \left\{ -\psi_x + a_L \psi_x^3 + a_T \psi_x \psi_y^2 \right\} \\ \frac{\partial \psi_y}{\partial \tau} &= -\frac{\epsilon^2}{2} \left\{ -\psi_y + a_L \psi_y^3 + a_T \psi_y \psi_x^2 \right\},\end{aligned}\quad (3)$$

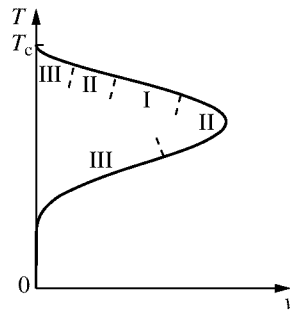
where

$$\begin{aligned}a_L &= 1 + \frac{(r(T_c - T))^{1/2} \kappa^{1/2}}{\gamma r_4} \left[ \frac{-R_L}{8} - \frac{R_L^2}{2r(T_c - T)} \right] \\ a_T &= 3 + \frac{(r(T_c - T))^{1/2} \kappa^{1/2}}{\gamma r_4} \left[ -R_T - \frac{4R_T^2}{r(T_c - T)} \right],\end{aligned}\quad (4)$$

$\tau = (Mr(T_c - T)/\kappa)t$  is a dimensionless time parameter, and  $\gamma$  is the surface energy per unit area,  $R_L$  and  $R_T$  are characteristic elastic energies. The steady state solution of Eqs.(3) depends on parameters  $a_L$  and  $a_T$ . If  $a_L < a_T$ , the stable steady state solution is a 1D composition-modulated structure,  $\psi_x = a_L^{-1/2}$  and  $\psi_y = 0$  or  $\psi_y = a_L^{-1/2}$  and  $\psi_x = 0$ . If  $a_L > a_T$ , the stable steady state solution is a 2D modulated structure,  $\psi_x = \psi_y = (a_L + a_T)^{-1/2}$ . If  $a_L + a_T < 0$  or  $a_L < 0$ , Eqs.(3) do not have stable steady state solutions. This means that the final structure has a finite modulation amplitude already near the onset of instability.

The pattern selection is governed by the interplay of elastic and surface energies. Let the surface energy be very high,  $\gamma \rightarrow \infty$ . Then the surface remains flat even in the non-linear regime;  $a_L = 1$ ,  $a_T = 3$ , which favors a 1D structure. There is a similarity with alloy decomposition in the bulk [6], where the resulting structure is a mixture of two phases with compositions  $c_1$  and  $c_2$ . A two-phase system is consistent with 1D structure and inconsistent with 2D structure. For a moderate  $\gamma$ , the effect of surface corrugation becomes important, which alters  $a_L$  and  $a_T$  and favors 2D structure. This is similar to the case of lattice-mismatched systems where a 2D corrugation gives a more efficient elastic relaxation than a 1D one [7]. For a low surface energy,  $a_L < 0$ ,  $a_T < 0$ , and the final structure has a finite amplitude near the onset of instability. Since the interplay of elastic and surface energies depends on  $T_c - T$  (Eq.(4)), this yields a phase diagram on Fig. 2. Similar interplay between 1D and 2D structures persists in case of anisotropic surface mobility.

To conclude, we have shown that the alloy growth in open systems can result in both 1D and 2D modulated structure and the orientation of the structure is determined by growth temperature and growth velocity. Principle results, obtained for binary alloys, remain valid for ternary and quaternary alloys. This explains the 1D structure in InAlAs modulated in [110]-direction [8], the 1D structure in MgZnSs modulated in [100]-direction [9], and the 2D structure in GaInAsP modulated in [100] and [010]-directions [10].



**Fig. 2.** The phase diagram of final composition-modulated structure near the onset of instability. I: 1D structure, II: 2D structure, III: no solutions in the weak segregation regime, the structure has a finite amplitude.

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