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Equilibrium composition-modulated structures in epitaxial films of semiconductor alloys

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Spontaneous formation of composition-modulated structures is a common phenomenon in III–V and II–VI semiconductor alloys [1]. There exist two distinct possibilities for the formation of such a structure. Firstly, *equilibrium domain structures* can be formed in *closed systems*. This is realized by long-time growth interruption or by post-growth annealing. Thermodynamics can be applied to describe equilibrium structures which meet the condition of the Helmholtz free energy minimum. Secondly, *non-equilibrium structures* can be formed in *open systems*. These structures are governed by growth kinetics.

Although most of observed composition-modulated structures in semiconductor alloys correspond to as-grown samples, there is a possibility for the formation of modulated structures via annealing. E. g., experiments on non-stoichiometric As-rich GaAs show the *enhancement of bulk diffusion* of As atoms under annealing and the growth of nanometer-size As clusters [2]. These data make the problem of equilibrium modulated structures in semiconductors, which can be obtained under annealing, to be a problem of both experimental and theoretical interest.

Here we study the thermodynamic stability of an alloy $A_{1-c}B_cC$ in the epitaxial film against fluctuations of alloy composition. We consider a film on the (001)-substrate of a cubic crystal and we focus on the situation where the *homogeneous alloy with the composition* $c = \bar{c}$ is *lattice-matched to the substrate*. Both the substrate and the epitaxial film are *elastically-anisotropic cubic crystals having equal elastic modulus tensors*.

The free energy of an inhomogeneous alloy is a sum of the chemical and elastic contributions, $F_{\rm inh} = F_{\rm chem} + E_{\rm el}$, where $F_{\rm chem} = \int d^3\mathbf{r} f_{\rm chem}(c(x,y,z))$, and

$$F_{\rm el} = \frac{1}{2}\iint \frac{dk_x dk_y}{(2\pi)^2}\int_0^h dz \int_0^h dz' \,\widetilde{\Delta c}^{*}(k_x,k_y;z) B_{\rm el}(k_x,k_y;z,z')\widetilde{\Delta c}(k_x,k_y;z')\,. \tag{1}$$

Here $\widetilde{\Delta c}(k_x,k_y;z)$ is the Fourier transform of the composition fluctuation $\Delta c(x,y,z) \equiv c(x,y,z) - \bar{c}$, $z = 0$ is the interface plane, $z = h$ is the planar stress-free surface, elastic properties of the crystal are described through the kernel $B_{\rm el}(k_x,k_y;z,z')$ defined in [3], and the gradient energy ($\sim (\nabla c)^2$) [4,5] is omitted, since it is not important for alloy decomposition in the film [3]. The problem of finding the equilibrium profile of alloy composition consists of two parts. The first part is to find the criterion that the homogeneous alloy is absolutely unstable, i.e. *unstable against infinitesimal fluctuations of composition*. The second part is *to obtain the final equilibrium structure of the decomposing alloy*. The first problem was solved in [3], and the criterion of absolute instability is

$$\left(\frac{\partial^2 f_{\rm chem}(c;T)}{\partial c^2}\right) + \lambda_0^{\rm min} < 0\,. \tag{2}$$

Here $\lambda_0^{\min} = \min\limits_{k_x,k_y} \lambda_0(k_x,k_y)$, and $\lambda_0(k_x,k_y)$ is the minimum eigenvalue of the operator $\widehat{B}_{\mathrm{el}}$ for a given $\mathbf{k} = (k_x,k_y)$. The minimum eigenvalue $\lambda_0(k_x,k_y)$ is governed by the anisotropy of the elastic modulus tensor and is attained for wave vectors along the elastically soft direction [100] or [010]. The value $\lambda_0^{\min}$is attained asymptotically as $kh \to \infty$. Fluctuations of composition corresponding to the "soft mode" are localized at the surface $z = h$ and decay away from the surface,

$$\Delta c_{\text{soft mode}}(x,y,z|\mathbf{k}) \sim \exp[-|k_x|(h-z)]\exp(ik_x x) \ , \ |k_x|h \gg 1 \ , \ k_y = 0 \, , \tag{3}$$

and similar expression is valid for the "soft mode" with $\mathbf{k} = (0,k_y)$. At high temperatures, the left hand side of Eq. (2) is positive for all compositions. The temperature T_c and the composition c_0 where the l.h.s. of Eq. (2) vanishes for the first time correspond to the critical point of alloy instability in the epitaxial film.

The final structure of decomposing alloy was found numerically in [6], where the model regular solution approximation [7] was used for the chemical free energy of an alloy. An equilibrium structure was found, but neither the miscibility curve, nor the dependence of the period on temperature were obtained in [6].

Here, to obtain the *final equilibrium structure of the decomposing alloy* we focus on the vicinity of the critical point, i.e., on $T \approx T_c$ and $c \approx c_0$, and use the Ginzburg–Landau type of expansion of F_{inh}. We take the composition fluctuation is *a linear combination of soft modes* of the form of Eq. (3). Since numerical calculations show composition profile to be *one-dimensional*, we focus on composition modulation in the x direction. By taking into account the asymptotic behavior of the eigenvalue of $\widehat{B}_{\mathrm{el}}$ for soft modes [3], $\lambda_0(k_x,0) = \lambda_0^{\min} + B_1\exp(-2|k_x|h)$, one obtains the expansion for $\Delta F = F_{\mathrm{inh}} - F_{\mathrm{hom}}$ as follows,

$$\begin{aligned}\Delta F = \int_0^h dz \int dx \Bigg\{ & \left[\frac{1}{2}\left(\frac{\partial^2 f_{\mathrm{chem}}}{\partial c^2}\right)(c(\mathbf{r})-c_0)^2 - \frac{1}{2}\alpha\tau(c(\mathbf{r})-c_0)^2 + \frac{1}{4}D(c(\mathbf{r})-c_0)^4\right] \\ & - \left[\frac{1}{2}\left(\frac{\partial^2 f_{\mathrm{chem}}}{\partial c^2}\right)(\bar{c}-c_0)^2 - \frac{1}{2}\alpha\tau(\bar{c}-c_0)^2 + \frac{1}{4}D(\bar{c}-c_0)^4\right] \Bigg\} \\ & + \frac{1}{2}\int \frac{dk_x}{(2\pi)} \int_0^h dz \left[\lambda_0^{\min} + B_1 \exp\left(-2|k_x|h\right)\right] |\widetilde{\Delta c}(k_x,0;z)|^2 \, . \end{aligned} \tag{4}$$

Here $\tau = (T_c - T)/T_c \ll 1$, $\alpha = -T_c(\partial^3 f_{\mathrm{chem}}/\partial T \partial^2 c)$, $D = \frac{1}{6}(\partial^4 f_{\mathrm{chem}}/\partial c^4)$. We seek the composition profile as a periodic function $\Delta c(x,y,z) = \sqrt{2\alpha/D}\sqrt{\tau}\varphi(x,z)$. Here φ is combination of soft modes of Eq. (3) corresponding to composition modulation in x-direction with the period d_x. By substituting $\Delta c(x,y,z)$ of the above form into the free energy of Eq. (4), one obtains

$$\Delta F = Ah\frac{6\alpha^2\tau^2}{D}\left[\frac{1}{k_x^{(0)}h}J + 2\frac{B_1\exp(-2k_x^{(0)}h)}{\alpha\tau(2k_x^{(0)}h)}|a_1|^2\right] \, , \tag{5}$$

where A is the substrate area, and

$$J = k_x^{(0)2}\int_{-\frac{d_x}{2}}^{\frac{d_x}{2}} dx \int_0^h dz \left[\frac{1}{2}\left(-1+3\eta^2\right)\varphi^2(x,z) + \eta\varphi^3(x,z) + \frac{1}{4}\varphi^4(x,z)\right] \, . \tag{6}$$

Here η is proportional to the deviation of the average alloy composition $\bar{c}$ from the critical composition c_0, $\eta = (\bar{c} - c_0)/\sqrt{\tau}$; a_1 is amplitude of the first Fourier harmonic of φ. It follows from Eq. (6) that J does not depend on $k_x^{(0)}$. Minimization of ΔF from Eq. (5) with respect to $k_x^{(0)}$ shows that the second term in Eq. (5) is small compared to the first one. It allows *to split the problem into two parts*, and to obtain the *composition profile within one period of the structure* first, and to find the *period* afterwards. This is the key advantage of using Landau–Ginzburg expansion of F_{inh} which enables us to proceed as compared to [6]. Similar advantage of using Landau–Ginzburg theory was emphasized in [8] for a related problem of equilibrium composition-modulated structures in *bulk samples* of quaternary alloys.

The lowering of the total free energy of the system due to fluctuations of composition, $\Delta F < 0$, means that the minimization of J from Eq. (6) yields a non-trivial solution providing $J < 0$. If $|\eta| < 1/\sqrt{3}$, the quadratic coefficient in Eq. (4) is negative, i.e. the alloy is absolutely unstable. Then there obviously exists a solution which gives $J < 0$. The equation $\eta = \pm 1/\sqrt{3}$ yields *the spinodal curve* of the alloy epitaxial film near the critical temperature T_c. Due to cubic terms in J, a solution providing $J < 0$ may exist also in a certain region of η where $|\eta| > 1/\sqrt{3}$. The value $|\eta| = \eta^*$, where the solution providing $J < 0$ ceases to exist, corresponds to *the miscibility curve*. If $|\eta| > \eta^*$, the homogeneous alloy epitaxial film is absolutely stable. If $1/\sqrt{3} < |\eta| < \eta^*$, the homogeneous alloy epitaxial film is metastable. Numerical minimization of J yields the final structure of the alloy within one period. The form of the structure is close to one obtained in shcha. The modulation amplitude is maximum at the surface and decays away from the surface. Analysis of J versus η yields $\eta^* = 0.784$, i.e. it gives *the miscibility curve in the vicinity of the critical point*,

$$T_{\text{miscibility}}(\bar{c}) = T_c - \frac{T_c}{\eta^{*2}}(\bar{c} - c_0)^2 . \tag{7}$$

Then, given J, the criterion of the minimum with respect to $k^{(0)}h$ reads

$$\frac{\exp(2k^{(0)}h)}{(k^{(0)}h)} = \frac{B_1}{\alpha\tau(-J)}|a_1|^2 . \tag{8}$$

To calculate the period d, we take, as an example, $\mathrm{GaAs}_{1-c}\mathrm{Sb}_c$ where $T_c = 740$ K [3]. Evaluation of d from Eq. (8) yields, for $T_c - T = 10$ K, $d = 1.4h$, for $T_c - T = 100$ K, $d = 2.0h$. Thus, the period is a weak logarithmic function of $(T_c - T)$ and is of the order of the film thickness h.

With further lowering of T, all modes of fluctuations contribute to the equilibrium structure. To estimate the miscibility curve at arbitrary T, we use the ansatz of [9], where composition is independent of z, $\Delta c(x, y, z) = c_1(x)$. If we construct a curve which bounds the region on $T - c$ phase diagram corresponding to alloys unstable against such a fluctuation, this curve will lie inside the exact miscibility curve. The equilibrium phase diagram of alloy epitaxial film is shown in Fig. 1.

To conclude, we have solved a *non-linear problem* for the final equilibrium structure of phase-separating alloy in an epitaxial film in the vicinity of the critical point. The *exact phase diagram* in variables "temperature – average composition" is constructed, containing the region of absolutely unstable, metastable, and stable alloys. The *period* of equilibrium structure is found. An equilibrium composition-modulated structure with a

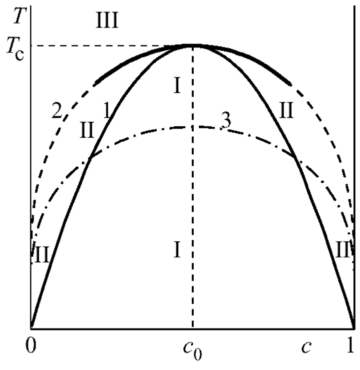

Fig 1. Equilibrium phase diagram of an alloy in the epitaxial film. $(c_0; T_c)$ is the critical point of alloy instability against spinodal decomposition. 1 is the spinodal curve; the solid part of the curve 2 is the calculated miscibility curve (Eq. (7)); the dashed part of the curve 2 is the schematic miscibility curve for arbitrary temperatures; 3 is the miscibility curve calculated by the ansatz of Glas [9]. (I) is the region of the absolutely unstable alloys, (II) is the region of metastable alloys, and (III) corresponds to stable alloys.

one-dimensional periodicity in the surface plane is a *spontaneously formed quantum-wire superlattice.*

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