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Non-linear theory of alloy phase separation in open systems: Kinetic phase transitions between 1D and 2D structures

V. A. Shchukin and A. N. Starodubtsev

Ioffe Physico-Technical Institute, St Petersburg, Russia

Spontaneous formation of nanometer-scale composition-modulated structures is a common phenomenon for III–V and II–VI semiconductor alloys [1]. These structures are mostly being formed in open systems during the epitaxial growth. Theoretical understanding has so far been achieved of earlier stages of growth where the linear stability analysis of the homogeneous alloy growth applies [2–4]. In semiconductors, bulk diffusion coefficients are, typically, negligibly small compared to surface ones. Then, fluctuations of composition are created at every surface atomic layer and are frozen once this layer is overgrown by subsequent layers. Frozen fluctuations of composition from the entire film affect, via long-range strain fields, migration of surface adatoms. This interaction can result in a kinetic instability of a homogeneous alloy growth against fluctuations of composition. However, to describe a final structure formed during the growth, a non-linear theory is needed.

In our earlier paper [5] we have solved a non-linear problem for the final structure of a growing alloy in a *weak segregation regime* close to the onset of the instability, i. e. in the vicinity of the solid line at the linear stability phase diagram of Fig. 1(a). In the diagram of
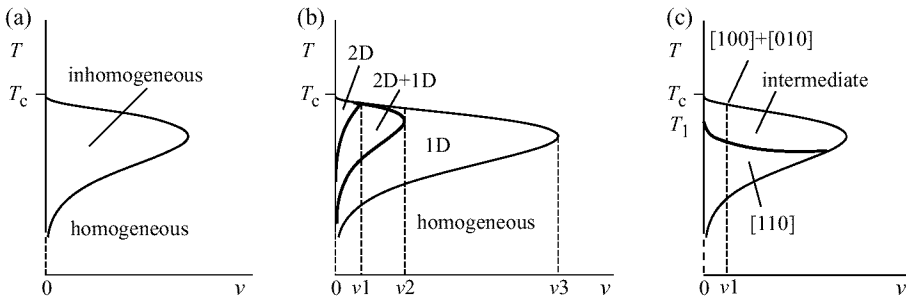

Fig. 1. Phase diagram of the alloy growth. T is growth temperature, and v is growth velocity. (a) Linear stability diagram. Surface diffusion is isotropic. (b) Steady-state diagram containing the regions of homogeneous growth, of the growth of a 1D structure, of the growth of a 2D structure, and the region where the stable growth of both 1D and 2D structures is possible. Surface diffusion is isotropic. (c) Linear stability diagram. Surface diffusion is anisotropic. Directions of the wave vectors of the most unstable modes of composition fluctuations are indicated.

Fig. 1(a), at high temperatures T, the instability is hindered by the mixing entropy of the alloy. At low T, the surface diffusion coefficient decreases, $D(T) = D_0 \exp(-E_a/k_B T)$, where E_a is the activation energy. Then adatoms are buried by the incoming flux faster than migrate along the surface, that hinders the instability. Due to elastic anisotropy of zinc-blend semiconductors, the instability occurs for the first time, for the growth on a (001) substrate, for composition fluctuations with the wave vector in an elastically soft direction [100] or [010]. The solution of a non-linear problem in a weak segregation regime [5] shows a principal possibility of the formation of either a 1D structure modulated along [100] or along [010] or a 2D structure modulated in both [100] and [010] directions. However, a

2D structure occurs only in a very narrow temperature interval which is hard to realize experimentally.

Intending to explain the formation of commonly observed 2D modulated structures, in the present paper we seek the final state of the alloy growth in a *strong segregation regime*, i.e., in the entire region of the $T-v$ phase diagram where the homogeneous growth is unstable. We consider the growth of an alloy $A_{1-c}B_cC$ by molecular beam epitaxy (MBE) on an atomically rough surface. The alloy is *lattice-matched on average* to the (001) substrate. The growth proceeds via deposition of atoms on the surface, surface migration of atoms in a stress- and composition-dependent chemical potential, and incorporation of atoms into the growing crystal, desorption being neglected. Let the composition equal $c(\mathbf{r}) = \bar{c} + \phi(\mathbf{r})$, the average composition being $\bar{c} = 1/2$, and the surface profile equal $h(x, y) = vt + \zeta(x, y)$, where v is the average growth velocity controlled by the deposition flux. Coupled kinetic equations describe a joint evolution of composition fluctuations $\phi(\mathbf{r})$ at the advancing surface and of the surface profile fluctuations $\zeta(x, y)$,

$$\frac{\partial \zeta}{\partial t} = a \frac{D_{ij}^{S}}{k_B T} \nabla_i \nabla_j \left[a \frac{\delta F}{\delta \zeta} - \phi \frac{\delta F}{\delta \phi} \right]$$

$$\frac{\partial \phi}{\partial t} = \frac{D_{ij}^{c}}{k_B T} \nabla_i \nabla_j \frac{\delta F}{\delta \phi} - \left[v + \frac{\partial \zeta}{\partial t} \right] \frac{\phi}{a} . \tag{1}$$

Here F is the total Helmholtz free energy, D_{ij}^{S} is the diffusion coefficient tensor related to the evolution of the surface, D_{ij}^{c} is the one related to the substitutional diffusion of alloy components on the surface, and a is the lattice parameter.
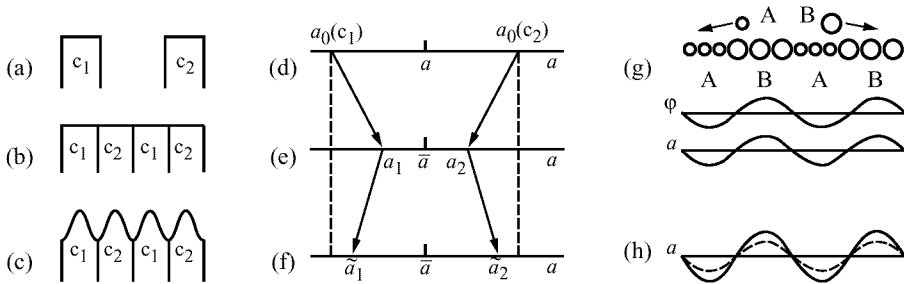

Fig. 2. Coupling between composition modulation and surface profile. (a) Two separate bulk alloys; (b) Composition-modulated structure with the planar surface; (c) Composition-modulated structure with a non-planar surface; (d) Lattice parameters of bulk alloys with compositions c_1 and c_2; (e) Lattice parameters of coherently conjugated composition domains in a stressed system with the planar surface; (f) Lattice parameters of coherently conjugated domains in a partially relaxed system with a non-planar surface; (g) Elastic driving force to phase separation: atoms A(B) are attracted by A(B)-rich domains; modulation of composition ϕ and of the lattice parameter a; (h) modulation of the lattice parameter at the planar surface (dashed line) and at a non-planar surface (solid line).

For the lattice-matched alloy growth, the composition instability and the morphological one are not coupled in a linear regime [3, 5]. A key property of the non-linear regime is that *both instabilities are coupled* (Fig. 2). Let the structure consist of alternating domains with compositions $c_1 < \bar{c}$ (A-rich domains) and $c_2 > \bar{c}$ (B-rich domains) and the binary AC have smaller lattice parameter than BC. Then, for bulk alloys $A_{1-c_1}B_{c_1}C$ and $A_{1-c_2}B_{c_2}C$, one has $a_0(c_1) < \bar{a} \equiv a(\bar{c}) < a_0(c_2)$ (Fig. 2(d)). In the structure of Fig. 2(b), domains

are coherently conjugated. Then, A-rich domains are stretched with respect to intrinsic lattice parameter of bulk $A_{1-c_1}B_{c_1}C$, i.e. $a(c_1) > a_0(c_1)$. At the same time, they are compressed with respect to the average lattice parameter of the structure $\bar{a}$. B-rich domains are compressed with respect to the lattice parameter of bulk $A_{1-c_2}B_{c_2}C$, and stretched with respect to $\bar{a}$. The surface consists of alternating domains under tensile and compressive stress and is unstable against undulations, if the modulation wavelength exceeds a certain critical value. Then the energy gain due to elastic relaxation exceeds the energy cost of a non-planar surface profile, and the surface will consist of troughs over domain boundaries and crests in the center of each composition domain (Fig. 2(c)). Due to elastic relaxation, lattice parameters of A-rich and B-rich domains are shifted towards their intrinsic values, $a_0(c_1)$ and $a_0(c_2)$ (Fig. 2(f)).

Figures 2(g) and 2(h) illustrate the *reaction* of surface undulations on phase separation. Atoms B having larger atomic radius prefer to incorporate to surface regions which are stretched *with respect to the average lattice parameter* $\bar{a}$, i.e., to B-rich domains (see, e.g., [4]). Similarly, A atoms prefer to incorporate to A-rich domains. Elastic driving force to phase separation is proportional to the actual variation of the lattice parameter, $a(c_2) - a(c_1)$. Since this variation increases due to surface undulations (Fig. 2(f)), the elastic driving force to phase separation increases, too.

To obtain stable steady-state solutions of kinetic equations (1), we have solved these equations numerically and have checked the stability of solutions by integration of kinetic equation over time in the vicinity of the steady state solutions.

Figure 1(b) displays the calculated steady-state phase diagram of the alloy growth in case of isotropic surface diffusion. The modulation period is known to increase with the decrease of the growth velocity v [6]. The interplay between surface and elastic energies favors surface undulations at large period, i.e., at low v. A non-planar surface favors a 2D structure modulated in both [100] and [010] directions versus a 1D structure modulated in either [100] or [010] direction. The effect is similar to that for strained islands in lattice-mismatched systems where 2D structures (pyramids) provide a more efficient elastic relaxation than 1D structures (prisms) [7]. The diagram contains the regions of the homogeneous growth, of the growth of 1D structures, of the growth of 2D structures, and the region where both 1D and 2D structures can grow. In the latter region, the actual final structure of the growing alloy depends on initial conditions. To obtain the structure for any particular initial conditions, one needs to integrate kinetic equations (1) over the entire time of evolution. We do not address this problem here.

In Fig. 1(b) we use typical material parameters for III–V semiconductors. Elastic moduli are $c_{11} = 1.0 \times 10^{12}$ erg/cm^3, $c_{12} = c_{44} = 0.5c_{11}$, the surface energy is 50 meV/Å^2; the lattice mismatch between pure AC and BC is 7%; the critical temperature is $T_c = 1000$ K, the activation energy for surface diffusion is $E_a = 1.5$ eV. Growth velocities marked in Fig. 1(b) are: $v_1 = 1.2$ Å/s, $v_2 = 4.0$ Å/s and $v_3 = 96$ Å/s. The growth velocity v_3, at which the instability is suppressed, is higher than typical ones in MBE. The growth velocities v_1 and v_2 corresponding to the kinetic phase transition between the growth of a 1D structure and the growth of a 2D structure, are just of the order of typical ones in MBE. Thus, the described kinetic phase transition corresponds to realistic growth velocities and can indeed be observed.

A kinetic phase transition between the growth of a 1D structure and the growth of a 2D one has been observed by Ueda *et al.* [8] in the MBE growth of InAlAs alloy lattice-matched to InP(001) substrate. At the growth velocity $v = 3$ Å/s, the growth temperature has been varied. At 440 and 470 °C, a 1D modulation in [110] direction is formed. The growth at

higher temperatures, 500, 530 and 560 °C reveals a 2D modulated structure in [100] and [010] directions.

To address this experiment we take into account the anisotropy of the surface diffusion ($D_{[\bar{1}10]} \neq D_{[110]}$) and construct the linear stability phase diagram of Fig. 1(c). At high temperatures, close to the onset of instability, the interval of wave vectors $\mathbf{k}_{\parallel}$ of unstable fluctuations is rather narrow. Then, the wave vectors of the most unstable fluctuations $\mathbf{k}_{\parallel}^{(0)}$ are parallel to elastically soft directions [100] and [010]. As the temperature decrease, the interval of $\mathbf{k}_{\parallel}$ corresponding to unstable fluctuations becomes wider, the role of elastic anisotropy decreases, and the role of diffusion anisotropy increases. The orientation of $\mathbf{k}_{\parallel}^{(0)}$ deviates from [100] and [010] towards the direction of fast diffusion [110].

Finally, the direction of $\mathbf{k}_{\parallel}^{(0)}$ coincides with [110]. In this case, the growth will presumably result in a 1D modulated structure. Calculated phase diagram of Fig. 1(c) is in qualitative agreement with experimental results. A detailed consideration given in Ref. [9], allows to reach a quantitative agreement and to fit the kinetic phase transition temperature T_1.

To conclude, the steady state phase diagram of Fig. 1(b) applies to any alloy. We explain a large variety of structures, e. g., the 1D structure in InAlAs modulated along [110] [10], the 2D structure in InGaAsP modulated in [100] and [010] directions [11], and a kinetic phase transition in InAlAs between the growth of a 2D structure modulated along [100] and [010] and the growth of a 1D structure modulated along [110] [8]. Our results demonstrate a possibility to tune the structure between 1D and 2D ones by varying growth velocity and temperature.

Acknowledgements

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