

Kinetic instability of semiconductor alloys *

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Received 15 October 2003, accepted 10 April 2004

Abstract

Semiconductor alloy epitaxial films grown in immiscibility region demonstrate at some temperatures and compositions the tendency to decompose into the periodic composition modulated structures (superlattices). Modulated structures occur in the process of the film growth in open system.

We suggest a concept of semiconductor alloy decomposition due to a kinetic phase transition from the growth regime of the homogeneous alloy to the growth of the composition modulated structure.

Kinetic instability is promoted by the drift of adatoms in the field of an elastic driving force created according to Vegard's rule by the "frozen" fluctuations of composition in already completed thickness of the film.

For particular growth mechanism, we focus on the step flow growth of the film from the vapour on the vicinal to [001] surface of cubic substrate. Temperature of decomposition is shown to increase with the increase of elastic effects. The elastic anisotropy is taken into account. The in-plane wave vectors of the most unstable mode of composition fluctuations differ from elastically soft directions. It opens a possibility for formation of superlattices oriented in arbitrary directions.

Room temperature lasing in laser diodes on the base of modulated structure of InGaAsP alloy has been achieved by I.S. Tarasov from Ioffe Institute RAS.

PACS: 81.15.Aa, 68.65.Cd

*Presented at Russian-Israeli Conference *Frontiers in Condensed Matter Physics*. Shores, Israel, 19-24 October 2003

Spontaneously formed macroscopic composition-modulated structures have been observed in numerous alloys of III-V and II-VI semiconductors grown by MBE, MOCVD, VPE, and LPE (for a review see, e. g., [1]). Conventional attempts to explain the phenomenon have used the concept of spinodal decomposition of an alloy [2, 3]. The thermodynamic theory of [2, 3] developed for metal alloys deals with *closed systems* where the alloy can lower its free energy by the formation of a composition-modulated structure. The kinetics of the spinodal decomposition [3] describes the evolution of an alloy from the initial homogeneous state, which is quenched to a temperature where it is thermodynamically unstable, to a final equilibrium state, representing the alloy with spatial modulation of composition.

Although the theory of [2, 3] can be extended to bulk samples and epitaxial films of semiconductor alloys [4], one should emphasize the basic difference between formation mechanisms and observation conditions of composition-modulated structure in metal alloys, on the one hand, and those in semiconductor alloys, on the other hand. *i)* The formation of composition-modulated structures in metal alloys occurs in *closed systems* under a long time annealing (aging). For typical temperatures of aging, $T \approx 600 - 1000^{\circ} \text{C}$, characteristic values of bulk diffusion coefficients are of the order of $D \approx 10^{-11} - 10^{-8} \text{ cm}^2\text{s}^{-1}$. These diffusion coefficients are sufficiently large to promote the formation of composition-modulated structures on an accessible time scale. *ii)* Composition-modulated structures in semiconductor alloys are observed in *as-grown* samples which implies that these structures are being formed in *open systems* in the process of crystal growth. Bulk diffusion coefficients in semiconductors at typical growth temperatures ($T \approx 600^{\circ} \text{C}$) are of the order $D \approx 10^{-19} - 10^{-16} \text{ cm}^2\text{s}^{-1}$ [5]. These diffusion coefficients are too small to develop a composition-modulated structure during the growth time, and another kinetic mechanism than the bulk migration of atoms is needed for the structure formation.

In the present paper we study the instability which may occur in an *open system* in the process of growth of a binary alloy $A_{1-c}B_c$, and our treatment is applicable also to the growth of a ternary semiconductor alloy $A_{1-c}B_cC$. The focus is given on the instability of the alloy growth with respect to composition fluctuations δc . The theory linear in δc is developed, and the criterion is found that the amplitude of composition fluctuation increases with the epitaxial film thickness. This means that the growth of a homogeneous alloy is unstable, and the growth may result in an alloy with a spatial modulation of composition.

We consider the growth of an alloy from the vapour phase. We study epitaxial film on a substrate where the layers from the 1st to the M th are

completed, and the $(M+1)$ -st layer is the growing one. Growth on atomically smooth surfaces proceeds via the surface migration of adatoms and via their incorporation into the growing layer. In the process of growth of each L th layer ($1 \leq L \leq M$), there occurs the fluctuation of alloy composition $\delta c(\mathbf{r}; L)$, where $\mathbf{r} = (x, y)$ is the two-dimensional position vector. Since we neglect the migration of atoms in the bulk, the composition fluctuations are “frozen” after the given layer is covered by subsequent layers.

First, “frozen” fluctuations of composition in the top completed M th layer, $\delta c(\mathbf{r}; M)$, affect the migration of adatoms in the next, growing, $(M+1)$ -st layer via a short-range potential $U_{sr}^{(A,B)}(\mathbf{r}; M+1)$ acting on adatoms A and B. Second, “frozen” fluctuations in all completed monolayers $1 \leq L \leq M$ create, in accordance with the Vegard’s rule, the long-range strain field. Therefore a long-range potential $U_{lr}^{(A,B)}(\mathbf{r}; M+1)$ appears which is proportional to the strain tensor at the surface ε_{ij} . The total potential acting on adatoms is the sum of short-range and long-range terms,

$$U^{(A,B)}(\mathbf{r}; M+1) = V_{sr}^{(A,B)} \delta c(\mathbf{r}; M) + V_{lr}^{(A,B)} \varepsilon_{ij}(\mathbf{r}; z) \Big|_{z=Ma}, \quad (1)$$

where the coefficients $V_{lr}^{(A,B)}$ may be called *deformation potentials* of the adatoms A or B, and a is the lattice parameter. The strain tensor may be given in terms of the static Green’s tensor $G_{ij}(\mathbf{r} - \mathbf{r}', z, z')$ of the elasticity theory for a semi-infinite medium, found in Ref. [6]. This relation reads

$$\begin{aligned} \varepsilon_{ij}(\mathbf{r} - \mathbf{r}', z) \Big|_{z=Ma} &= \\ &= \left(\frac{\partial a}{\partial c} \right) \sum_{L=1}^M \frac{1}{2} \left[\nabla_i \nabla'_p G_{jp}(\mathbf{r} - \mathbf{r}', z, z') + \nabla_j \nabla'_p G_{ip}(\mathbf{r} - \mathbf{r}', z, z') \right] \Big|_{\substack{z=Ma \\ z'=La}} \times \\ &\quad \times \delta c(\mathbf{r} - \mathbf{r}', L). \end{aligned} \quad (2)$$

The chemical potential of the rarified gas of adatoms on the surface is the sum of the potential $U^{A,B}$ and of the entropy term related to the areal concentration of adatoms $N^{(A,B)}$,

$$\mu^{(A,B)}(\mathbf{r}) = U^{(A,B)}(\mathbf{r}) - T \ln(a^2 N^{(A,B)}(\mathbf{r})). \quad (3)$$

The gradient of the chemical potential in the inhomogeneous system causes the surface flux of adatoms [7],

$$\mathbf{j}^{(A,B)}(\mathbf{r}) = -T^{-1} D^{(A,B)} \nabla \mu^{(A,B)}(\mathbf{r}), \quad (4)$$

where $D^{(A,B)}$ is the diffusion coefficient. By substituting the expression for the chemical potential, one gets the surface flux of adatoms as a sum of the diffusion and drift terms:

$$\mathbf{j}^{(A,B)}(\mathbf{r}) = -D^{(A,B)}\nabla N^{(A,B)}(\mathbf{r}) - T^{-1}N^{(A,B)}(\mathbf{r})D^{(A,B)}\nabla U^{(A,B)}(\mathbf{r}). \quad (5)$$

If there is an oversaturation in the gas phase, there occurs the flux of atoms from the gas to the surface characterized by the deposition rate $G_0^{(A,B)}$. The concentration of adatoms and surface fluxes of adatoms may be written as sums of equilibrium quantities $N_{eq}^{(A,B)}(\mathbf{r})$, $\mathbf{j}_{eq}^{(A,B)}(\mathbf{r})$ and excess non-equilibrium quantities $\Delta N^{(A,B)}(t; \mathbf{r})$, $\Delta \mathbf{j}^{(A,B)}(t; \mathbf{r})$ caused by the oversaturation. The excess surface flux $\Delta \mathbf{j}^{(A,B)}$ of adatoms may be written in terms of the excess areal concentration $\Delta N^{(A,B)}$ of adatoms as a sum of diffusion and drift contributions:

$$\begin{aligned} \Delta \mathbf{j}^{(A,B)}(t; \mathbf{r}) &= -D^{(A,B)}\nabla \Delta N^{(A,B)}(t; \mathbf{r}) \\ &\quad - T^{-1}D^{(A,B)}\Delta N^{(A,B)}(t; \mathbf{r})\nabla U^{(A,B)}(\mathbf{r}). \end{aligned} \quad (6)$$

The excess non-equilibrium areal concentration of adatoms $\Delta N^{(A,B)}(t; \mathbf{r})$ and the excess surface flux of adatoms $\Delta \mathbf{j}^{(A,B)}(t; \mathbf{r})$ obey the continuity equation:

$$\frac{\partial \Delta N^{(A,B)}(t; \mathbf{r})}{\partial t} + \text{div} \Delta \mathbf{j}^{(A,B)}(t; \mathbf{r}) = G_0^{(A,B)} - \frac{\Delta N^{(A,B)}(t; \mathbf{r})}{\tau_{desorption}^{(A,B)}}. \quad (7)$$

Here $\tau_{desorption}^{(A,B)}$ is the average desorption time. We emphasize here that the deposition and desorption terms in the right hand side of Eq. (7) are particular features of an open system.

The set of coupled equations (6), (7) allows to find the excess concentration of adatoms $\Delta N^{(A,B)}(t; \mathbf{r})$ and surface fluxes of adatoms $\Delta \mathbf{j}^{(A,B)}(t; \mathbf{r})$. Boundary conditions needed for these equations depend on the growth mechanism.

We focus on the step-flow growth on a surface vicinal to the (001) surface of a cubic crystal. A perfect vicinal surface displayed in Fig. 1 consists of (001) terraces of equal width d separated by steps. Each step consists of [110] straight sections of equal length l_K separated by kinks. It was shown in Ref. [8] that the crystal growth on such a surface proceeds via kink flow and step flow, it can be stable against step bunching and step meandering, and the perfect geometry of the vicinal surface persists during the growth.

We consider fluctuations of composition with the characteristic scale of inhomogeneity r_0 large compared to the spacing between kinks, and treat

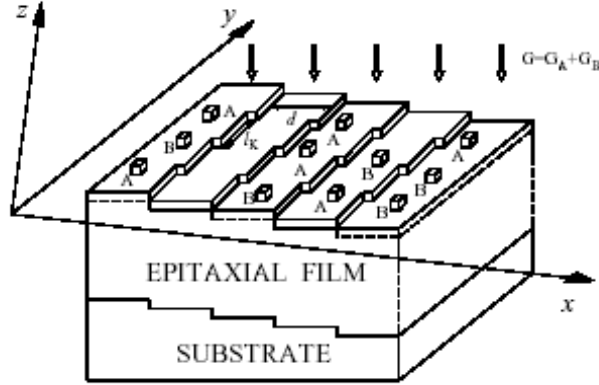


Figure 1: Growth of an alloy on a vicinal surface. Layers are defined in such a way that they repeat the stepped shape of the substrate. The dashed line depicts the top completed layer.

kinks as continuously distributed along steps (the so-called approximation of *continuous line sinks*). These sinks are asymmetric with respect to lower and upper terraces since the barrier for adatoms approaching the sink from the upper terrace is higher than that for adatoms on the lower terrace. Corresponding boundary conditions at the n th line sink positioned at $x = x_n = nd$ read:

$$\Delta N^{(A,B)} \Big|_{x=x_n+\eta} = 0, \quad \Delta \mathbf{j}^{(A,B)} \Big|_{x=x_n-\eta} = 0, \quad (8)$$

where $\eta \rightarrow +0$ [9].

The set of coupled equations (6),(7) with the boundary conditions (8) has been solved in the perturbation series with respect to the parameter U/T up to the first-order terms, and both $\Delta N(t; \mathbf{r})$ and $\Delta \mathbf{j}(t; \mathbf{r})$ have been calculated [10]. After the fluxes of both adatoms A and adatoms B attaching the line sink at the given point are known, it is possible to find the fluctuation of alloy composition $\delta c(\mathbf{r})$ which is being frozen at this point of the growing layer. The fluctuation $\delta c(\mathbf{r}; M + 1)$ formed after the completion of the $(M + 1)$ -st layer is found in the form of the linear response to the potential $U^{(A,B)}(\mathbf{r}; M + 1)$ acting on adatoms during the growth of the $(M + 1)$ -st layer.

The set of linear equations (6) - (8) describes the dependence of alloy

composition fluctuation $\tilde{\delta}c(\mathbf{k}; M)$ on the layer's number M :

$$\tilde{\delta}c(\mathbf{k}, M) = \frac{\bar{c}(1 - \bar{c})}{T} \times \left[Z(\mathbf{k})\tilde{\delta}c(\mathbf{k}, M - 1) + ka \sum_{s=1}^3 W_s(\mathbf{k}) \sum_{L=1}^{M-1} \exp[-\alpha_s ka(M - L)]\tilde{\delta}c(\mathbf{k}, L) \right]. \quad (9)$$

Here $Z(\mathbf{k})$ and $W(\mathbf{k})$ are short-range and long-range terms. It was shown in Ref. [10] that one may seek the solution in the exponential form $\tilde{\delta}c(\mathbf{k}; L) \sim \exp(\gamma kaL)$. Then the inequality $\text{Re}\gamma(\mathbf{k}) > 0$ yields the criterion that the fluctuation amplitude increases with the monolayer's number.

The mechanism responsible for this amplification is the drift of adatoms of the growing layer in the effective potential U created by the “frozen” fluctuations of alloy composition in the completed layers. The diffusion component of the surface flux of adatoms tends to smooth out fluctuations of composition. For high temperatures, diffusion dominates drift, and no amplification of fluctuation occurs. At a certain critical temperature T_c and at a certain wave vector \mathbf{k}_c , there occurs amplification of the fluctuation amplitude. This temperature is the temperature of *kinetic phase transition* between the growth of the homogeneous alloy and the growth of the alloy with spatial modulation of alloy composition. At temperatures below T_c , drift dominates diffusion, and there exists a region in the \mathbf{k} -space where fluctuations of composition increase from layer to layer.

The temperature T_c and the wave vector of the most unstable mode \mathbf{k}_c are determined by the interplay of several tendencies. First, the Green's tensor from Eq. (2) is determined by the symmetry of bulk elastic moduli. Second, the symmetry of the deformation potential $V_{lr\,ij}^{(A,B)}$ from Eq. (1) is determined by the symmetry of the surface. As a result of this interplay, any direction of the wave vector of the most unstable mode of composition fluctuations (“the soft mode”) can occur.

Calculations of the kinetic phase transition temperature show that T_c increases with the increase of adatom deformation potential. It means that, in contrast to the effect of long-range elastic forces on the thermodynamic instability of alloys, where they hinder the phase separation, they *favor kinetic instability*. The reason is that adatoms are attracted by domains of the surface with the excess concentration of like atoms, i. e., atoms with larger radius are attracted by domains which are under tensile strain, and smaller atoms are attracted by domains under compressive strain.

Fig. 2 displays the result of model calculations of $\text{Re}\gamma(\mathbf{k})$ which have been performed for $d = 100a$, $l_k = 10a$, isotropic deformation potential,

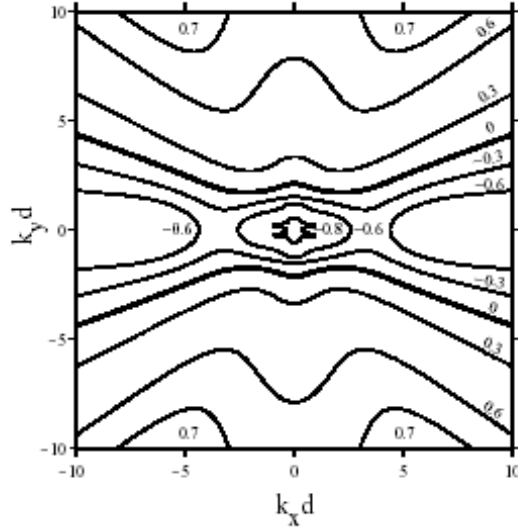


Figure 2: Amplification coefficient $\text{Re}\gamma(\mathbf{k})$ as a function of the 2D wave vector. Regions in the \mathbf{k} -space where $\text{Re}\gamma > 0$ correspond to unstable fluctuations. $d = 100a$, $l_k = 10a$, $D_{yy} = 5D_{xx}$, $W_{xx} = W_{yy}$.

anisotropic diffusion coefficient of adatoms ($D_{yy}^{(A)} = 5D_{xx}^{(A)}$, $D_{yy}^{(B)} = 5D_{xx}^{(B)}$), and $T = 0.7T_c$. There is a region of unstable modes with $\text{Re}\gamma > 0$ at small k_y satisfying the criterion $|k_y|l_K \ll 1$ which justifies the approximation of continuous line sinks.

To conclude, the kinetic mechanism is proposed of the amplification of alloy composition modulation with the thickness of the epitaxial film. *Long-range elastic interaction favors the kinetic instability and results in the increase of the kinetic phase transition temperature.* For different values of material parameters, one may expect the occurrence of composition-modulated structure with any other orientation.

The work was supported by Russian Foundation for Basic Research, Grants No. 03-02-04019; 03-02-17577a

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