ADP013159

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TITLE: Nanostructures: Physics and Technology International Symposium [9th], St. Petersburg, Russia, June 18-22, 2001 Proceedings

9th Int. Symp. "Nanostructures: Physics and Technology"
St Petersburg, Russia, June 18–22, 2001

NT.14p

Effect of the surface relaxation on spinodal decomposition of semiconductor epitaxial films

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Abstract. Semiconductor alloys are unstable at critical temperatures because of the positive enthalpy of alloy formation. The critical temperature of decomposition is the function of elastic parameters which differ due to structure relaxation of epitaxial film. It opens the new way to vary the critical temperature and the phase diagram.

There are numerous experimental data [1] which show that in the process of semiconductor alloy epitaxial growth there exist some temperature and composition intervals where semiconductor alloy is unstable, and decompose into periodic structures with composition modulations. The formation of such structures is possible due to the high value of surface diffusion coefficient (with respect to semiconductor bulk diffusion coefficient).

To explain the similar effect in the metal alloys Cahn [2] and Khachaturyan [3] suggested the theory of spinodal decomposition. Ipatova et al [4] have studied the spinodal decomposition of the thin epitaxial films of semiconductor alloys. It is showed that formation of periodic structures is defined by both the chemical energy and the elastic energy of semiconductor alloy caused by the composition fluctuations. However the phenomena of surface relaxation and reconstruction which change the crystal lattice structure near the growing surface have not been taken into account.

This paper deals with the effect of the surface relaxation on the critical temperature of spinodal decomposition. The surface relaxation means [5] that the surface crystalline plane atoms shift to the new equilibrium positions in a way that crystalline plane shifts as a whole in the direction normal to the surface. It leads to specific change of the lattice parameter in the direction of the normal. The surface crystalline planes of different orientation could relax either inward or outward. Some surface crystalline planes do not relax at all.

The semiconductor alloys are unstable at some temperatures because they have the positive enthalpy of formation. It means that at $T = 0$ K the composition modulated alloy corresponds to smaller Helmholtz free energy than homogeneous alloy.

Semiconductor alloys are disordered systems with composition fluctuations at each point

$$c(\mathbf{r}) = \bar{c} + \delta c(\mathbf{r}). \tag{1}$$

According to the Vegard's law, the lattice parameter fluctuated with composition (1). Coherent conjugation of regions with different lattice parameters requires elastic strains and results in specific elastic energy

$$\delta F_{\text{elastic}} = \frac{1}{2}\int dx dy \int_{-\infty}^{h} dz \lambda_{ijlm}\Big(\varepsilon_{ij}(\mathbf{r}) - \varepsilon_{ij}^{0}(\mathbf{r})\Big)\Big(\varepsilon_{lm}(\mathbf{r}) - \varepsilon_{lm}^{0}(\mathbf{r})\Big) \tag{2}$$

where $\varepsilon_{ij}^{0}(\mathbf{r})$ is the static intrinsic strains, λ_{ijlm} is the tensor of elastic moduli.

The elastic stress is equal by definition to

$$\sigma_{ij}(\mathbf{r}) = \frac{\partial f_{\text{elastic}}}{\partial \varepsilon_{ij}(\mathbf{r})} = \lambda_{ijlm}\Big(\varepsilon_{lm}(\mathbf{r}) - \varepsilon^{0}_{lm}(\mathbf{r})\Big). \tag{3}$$

It follows from Eq. (3) that the stress–free state corresponds to the strained state of the medium, $\varepsilon_{lm}(\mathbf{r}) = \varepsilon^{0}_{lm}(\mathbf{r}) \neq 0$. The local intrinsic strain is a linear function of composition fluctuations

$$\varepsilon^{0}_{ij}(\mathbf{r}) = \varepsilon^{0}_{ij}\delta c(\mathbf{r}), \qquad \varepsilon^{0}_{ij} = \begin{bmatrix} \varepsilon_{\parallel} & 0 & 0 \\ 0 & \varepsilon_{\parallel} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{bmatrix} \tag{4}$$

where ε^{0}_{ij} reflects the influence of relaxation on the symmetry of intrinsic strains. Disregarding surface relaxation: $\varepsilon^{0}_{ij} = \varepsilon_0\delta_{ij}$.

Semiconductor alloys consist of binary compounds of similar chemical nature. The mixture components have close chemical energies. As a result, the change of the chemical energy in semiconductor alloy is the same order of magnitude as the elastic energy (2). The total Helmholtz free energy equals

$$\delta F = F_{\text{inhom}} - F_{hom} = \delta F_{\text{elastic}} + \delta F_{\text{chem}}. \tag{5}$$

The requirement of total elastic energy minimum yields equilibrium equations of the theory of elasticity, such as the absence of external forces in the bulk and the boundary conditions of the absence of external stresses at the free surface. It is convenient to express the solution of these equilibrium equations in terms of the Green's tensor of the semi–infinite cubic elastic medium $G_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = G_{\alpha\beta}(x - x', y - y', z, z')$. This Green's tensor was found by Portz and Maradudin [6]. Finally we obtain the elastic free energy in the form:

$$\delta F_{\text{elastic}} = \frac{1}{2}\int d^3r d^3r' \delta c(\mathbf{r})\Big[\varepsilon^{0}_{\alpha\alpha}\lambda_{\alpha\alpha\beta\beta}\varepsilon^{0}_{\beta\beta}\delta(\mathbf{r}-\mathbf{r}') - A_{\alpha\beta}\frac{d}{dr_\alpha}\frac{d}{dr_\beta}G_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\Big]\delta c(\mathbf{r}') \tag{6}$$

where, considering the surface relaxation:

$$A_{\alpha\beta} = (c_{11}-c_{12})^2\varepsilon^{0}_{\alpha\alpha}\varepsilon^{0}_{\beta\beta} + c_{12}(c_{11}-c_{12})\Big(\sum_j \varepsilon^{0}_{jj}\Big)(\varepsilon^{0}_{\alpha\alpha}+\varepsilon^{0}_{\beta\beta}) + c_{12}^2\Big(\sum_{ij}\varepsilon^{0}_{ii}\varepsilon^{0}_{jj}\Big)\delta_{\alpha\alpha}\delta_{\beta\beta}, \tag{7}$$

(c_{11}, c_{12}, c_{44} being the elastic moduli in the Voigt notation). Disregarding surface relaxation: $A_{\alpha\beta} = (c_{11} - c_{12})^2\varepsilon_0^2\delta_{\alpha\alpha}$.

Since elastic properties of semi–infinite medium are homogeneous in the x- and y-directions in the substrate plain, it is convenient to use Fourier transformation in x and y and express the composition fluctuations as a linear combinations of static concentration waves with different $\mathbf{k}_{\parallel} = (k_x, k_y)$,

$$\delta c(\mathbf{r}) = \int \frac{d^2k_{\parallel}}{(2\pi)^2}\delta\tilde{c}(\mathbf{k}_{\parallel}, z)\exp\big(i(k_x x + k_y y)\big). \tag{8}$$

Substitution (8) into (6) results in

$$\delta F_{\text{elastic}} = \frac{S}{2}\int \frac{d^2k_{\parallel}}{(2\pi)^2}dz dz' \delta\tilde{c}(\mathbf{k}_{\parallel}, z)B_{\text{elastic}}(\mathbf{k}_{\parallel}, z, z')\delta\tilde{c}(\mathbf{k}_{\parallel}, z') \tag{9}$$

where S is the substrate area, the operator $\hat{B}_{\text{elastic}}(\mathbf{k}_{\|}, z, z')$ is equal to

$$B_{\text{elastic}}(\mathbf{k}_{\|}, z, z') = B_0 \delta(z - z') + \sum_{s=1}^{3} C_s(\Theta) k_{\|} \exp\big[-\alpha_s k_{\|} \mid z - z' \mid\big] +$$

$$+ \sum_{s'=1}^{3} \sum_{s=1}^{3} D_{ss'}(\Theta) k_{\|} \exp\big[-\alpha_s k_{\|}(h - z)\big] \exp\big[-\alpha_{s'} k_{\|}(h - z')\big]. \qquad (10)$$

The first and the second terms on the right–hand–side of Eq. (10) correspond to the operator $\hat{B}^{\infty}_{\text{elastic}}$ for an infinite cubic medium. The third term is the surface contribution to $\hat{B}_{\text{elastic}}$. The angel Θ is the angel between the direction of the wave vector $\mathbf{k}_{\|}$ and [100]–direction on the surface. The three dimensionless parameters α_s $(s = 1, 2, 3)$ describe the spatial attenuation of three static analogues of Rayleigh waves generated by static fluctuations of alloy composition. These parameters are defined in [6]. The coefficients $B_0, C_s, D_{ss'}$ are obtained here considering the surface relaxation, and they differ from the ones corresponding to surface relaxation disregarding in [4].

To derive the criterion of absolute instability it is convenient to present the variation of the Helmholtz free energy δF which is quadratic functional in $\delta c(\mathbf{k}_{\|}, z)$, in the diagonal form. Thereto we define the orthonormal eigenfunctions $\varphi_p(\mathbf{k}_{\|}, z)$ and eigenvalues $\lambda_p(\mathbf{k}_{\|})$ of operator $\hat{B}_{\text{elastic}}$ by the following equation:

$$\int_0^h B_{\text{elastic}}(\mathbf{k}_{\|}, z, z') \varphi_p(\mathbf{k}_{\|}, z') dz' = \lambda_p(\mathbf{k}_{\|}) \varphi_p(\mathbf{k}_{\|}, z) \qquad (11)$$

Expanding an arbitrary composition fluctuation $\delta c(\mathbf{r})$ in eigenfunctions $\varphi_p(\mathbf{k}_{\|}, z)$, one obtains the variation δF of the total Helmholtz free energy of the system in the diagonal form:

$$\delta F = \frac{S}{2} \int \frac{d^2 k_{\|}}{(2\pi)^2} \sum_{p=0}^{\infty} \Big[\Big(\frac{\partial^2 f}{\partial c^2} \Big) + \lambda_p(\mathbf{k}_{\|}) \Big] \mid a_p(\mathbf{k}_{\|}) \mid^2, \qquad (12)$$

$a_p(\mathbf{k}_{\|})$ being coefficients in expansion of $\delta \tilde{c}(\mathbf{k}_{\|}, z)$ in eigenfunctions $\varphi_p(\mathbf{k}_{\|}, z)$.

It follows from Eq. (2) that the operator $\hat{B}_{\text{elastic}}$ yields always a positive contribution to the variation of free energy. It means that all eigenvalues λ_p of the operator $\hat{B}_{\text{elastic}}$ are positive.

Due to mixing entropy at sufficiently high temperatures both bulk ternary III–V alloys and epitaxial films of alloys are stable, i.e. $\left(\partial^2 f / \partial c^2\right) > 0$, and the chemical free energy contribution to δF is positive. However the positive formation enthalpies of those alloys results in the fact that at sufficiently low temperatures $\left(\partial^2 f / \partial c^2\right) < 0$, and the chemical free energy decreases due to composition fluctuations. As a result, infinitesimal fluctuations of composition in the epitaxial film may lead to the decrease of the total Helmholtz energy, i.e. to $\delta F < 0$. This means the spinodal instability in the epitaxial film. The negative contribution of chemical free energy, $\left(\partial^2 f / \partial c^2\right) < 0$ to δF in Eq. (12) competes with the minimum of all positive eigenvalues of operator $\hat{B}_{\text{elastic}}$ denoted as λ_0^{min}. Then the thermodynamic criterion of the spinodal instability is as follows,

$$\frac{\partial^2 f}{\partial c^2} + \lambda_0^{min} = 0. \tag{13}$$

Equation (13) determines the critical temperature of spinodal instability T_c, the critical alloy composition and the wave vector $\mathbf{k}_\parallel^0$ of the "soft mode" responsible for the decomposition. The profile of composition fluctuations in this mode is described by the corresponding eigenfunction $\varphi_0(\mathbf{k}_\parallel^0, z)$.

The minimum eigenvalue $\lambda_0^{\rm min}$ of $\hat{B}_{\rm elastic}$ defining the critical temperature T_c became different as we consider the surface relaxation. It is shown that the outward relaxation conforms the elastic energy decrease thus the critical temperature of spinodal decomposition T_c is getting higher; on the contrary the inward relaxation increase the elastic energy and makes the critical temperature lower.

Since the effect of relaxation on the critical temperature of spinodal decomposition is different for different surfaces, it allows to operate the miscibility gaps and temperature T_c.

Acknowledgements

The work was supported, in different parts, by the Russian Federal Programs of Ministry of Industry, Science and Technology “Solid State Nanostructures”, project 97-2014 and “Surface Atomic Structures”, project 3.6.99.

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