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Growth rate and critical temperatures to avoid the modulation of composition of InGaAs epitaxial layers

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Ternary and quaternary semiconductor alloys are usually limited in their band gap engineering by problems related to modulation of composition. In this contribution, we point out the importance of the growth rate in the evolution of a modulation profile in epitaxial films. As a consequence, a diagram of phases for the epitaxial growth is proposed where a window of homogeneous composition is evidenced at low temperatures of growth. The model provides a framework for the epitaxial growth where temperature and growth rate regulation permits the control of the composition modulation in heteroepitaxies.
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The III–V semiconductor alloys continue to play an important role in the fabrication of opto- and microelectronics devices. To enhance properties such as carrier mobility or to obtain a specific band gap, it is necessary in many cases to choose ternary or quaternary semiconductor alloys. Generally, one assumes that these alloys with more than two components have a random atomic distribution in the bulk, without any type of order. However, these systems often present some type of long- or short-range order. Three different features can occur: (a) a random distribution of the atoms, (b) short range ordering in the unit cell, usually referred to as atomic ordering, and (c) modulated distribution, where the composition changes periodically. In general, such modulation significantly affects the electrical and optical properties of the layers considered and they exhibit smaller carrier mobility and broader photoluminescence peaks.[1] In this work, the importance of the deposition rate on the generation of modulation in heteroepitaxial layers is addressed.

The composition modulation in semiconductor alloys has generally been attributed to spinodal decomposition. Many different thermodynamic models have been reported previously[2–4] for estimating the critical temperature for the spinodal decomposition. All these models are based on Cahn's[5] theory for metals and have been extended for semiconductor heterostructures. These predicted critical temperatures based on thermodynamic instability are found to be much lower than the usual growth temperatures (see Table I) and are therefore in evident contradiction with experimental results.[6,7] Moreover, at usual heteroepitaxial growth temperatures, bulk diffusion cannot explain this growth-associated behavior because the diffusion occurs only at the surface.[8] Malishkin *et al.*[9] propose a model based on kinetic instability in 2D growth which is able to explain the modulation of composition experimentally observed at high growth temperatures. However, as we will see, the exhaustive development of the model establishes the existence of two modulation regimes depending on the growth conditions and the possibility of obtaining homogeneous alloys at low temperature.

Malishkin and Shchukin[9] incorporate the superficial diffusion effect during epitaxial growth into their thermodynamical analysis of the spinodal decomposition. The separation of phases occurs only in the superficial atomic layers (1 or 2 ML) where diffusion takes place, the buried layers remaining totally frozen. In this thin region with a thickness h_g, the composition of the modulated layer at equilibrium, δc_{eq}, is described as

$$\delta c_{\mathrm{eq}} = \overline{\delta c_{\mathrm{eq}}} \sin(k_{II} x), \tag{1}$$

where k_{II} is the modulation wavelength along the x direction contained in the growth plane and $\overline{\delta c_{\mathrm{eq}}}$ is the amplitude of modulation expressed as

$$\overline{\delta c}_{\mathrm{eq}} = \overline{\delta c^{\,0}} \exp[-\gamma k_{II}(h-z)]\exp(-\gamma k_{II} h), \tag{2}$$

where γ is a dimensionless factor that should be positive if the modulation progresses during the growth and z is the growth direction. The evolution of the concentration profile, δc, during the growth can be described by the Langevin equation:[10]

$$\frac{\partial \delta c}{\partial t} = -\frac{1}{T}\left[\nabla D^{*}\nabla\left(\frac{\delta F}{\delta c}\right)\right], \tag{3}$$

TABLE I. Critical temperature of spinodal decomposition for $\mathrm{In}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}$ using the model of Ref. 2[a] (T_c^s), Ref. 3[b], (T_c^G), Ref. 4[c], (T_c^I), and Ref. 9[d] (T_c^M). The alloys grown above these critical temperatures should be homogeneous.

	T_c^S (K)	T_c^G (K)	T_c^I (K)	T_c^M (K)
$\mathrm{In}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}$	−170	320	430	1030

[a] Reference 2.
[b] Reference 3.
[c] Reference 4.
[d] Reference 9.

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where F is the free energy of the system and D^* is the effective diffusion coefficient, which is constant and different from zero only in a superficial film of thickness h_g where diffusion occurs.

If we defined ωc as the deviation with respect to the modulation profile at equilibrium: $\omega c = \delta c - \delta c_{\text{eq}}$, the Langevin equation can be rewritten as

$$\frac{\partial \overline{\omega c}}{\partial t} = \frac{k_{II}^2 D^*}{T} A_0 \overline{\omega c} + \frac{k_{II}^2 D^*}{T}[A_0 + B_{nl}(\overline{\delta c_{\text{eq}}})]\overline{\delta c_{\text{eq}}} \tag{4}$$

where

$$A_0 = \frac{\partial^2 f}{\partial c^2} + B_0, \tag{5}$$

and $\overline{\omega c}$ is the amplitude of the Fourier component wave, *f*, the chemical free energy density and B_0 and $B_{nl}\,(\overline{\delta c_{\text{eq}}})$, the local and nonlocal elastic energy.[4]

Equation (4) describes the composition profile under diffusion in an epitaxial growth. At this point, Malishkin *et al.*[9] assume a new hypothesis: for the common growth temperatures, A_0 is so large that the first term of Eq. (5) does not produce a significant deviation of the modulation profile at equilibrium. That is to say, the atomic diffusion does not suppose any restriction in the formation of the modulated profile. We do not agree with this assumption and we therefore propose a more complete solution considering both terms of Eq. (4).

To make equation parameters adequate to experimental growth values, we propose the introduction of two new terms: first, the growth time, τ_g, defined as the time necessary to deposit a thickness h_g ($\tau_g = h_g / v_g$) where v_g is the growth rate. Second, the diffusion time, τ_d, defined as the average time of adatoms incorporation in the surface. The diffusion time is limited by the growth time and is defined by

$$\tau_d = \frac{1}{k_{II}^2 D}, \tag{6}$$

where D is the real diffusion coefficient. Moreover, the diffusion time, τ_d, is related to the growth temperature, *T*, according to the following expression:

$$\tau_d = \frac{1}{k_{II}^2 D_0} \exp\left(\frac{E_s}{kT}\right), \tag{7}$$

where E_s is the energy barrier of activation, *k* is the Boltzmann constant, and D_0 the preexponential factor of the diffusion coefficient. By equivalence with the second Fick law, we can replace D^* by the real diffusivity: $D = D^* A_0 / T$. Equation (4) then becomes

$$\frac{\partial \overline{\omega c}}{\partial t} = \frac{1}{\tau_d}(\overline{\omega c} - \overline{\delta c_{\text{eq}}}) + \frac{1}{\tau_d}\,\frac{B_{nl}(\overline{\delta c_{\text{eq}}})}{A_0}\overline{\delta c_{\text{eq}}}. \tag{8}$$

If the coefficients of this equation are independent of $\overline{\omega c}$, the solution becomes an ordinary differential equation. Integrating for a growth cycle, τ_g, to deposit a thickness, h_g, the solution is

$$\overline{\omega c} = \left(1 + \frac{B_{nl}(\overline{\delta c_{\text{eq}}})}{A_0}\right)\overline{\delta c_{\text{eq}}} + F(\tau_g, T), \tag{9}$$

where the function, $F(\tau_g, T)$, is defined as

$$F(\tau_g, T) = \exp\left(-\frac{\tau_g}{\tau_d}\right) = \exp\left[-\tau_g k_{II}^2 D_0 \exp\left(\frac{-E_s}{kT}\right)\right]. \tag{10}$$

Function F can oscillate between 0 and 1 if the deposition time, τ_g, is much larger than the diffusion time, τ_d, F trends to zero. In the inverse case, F reaches unity. The composition modulation is stable only when $\overline{\omega c} = 0$, and in consequence, Eq. (9) gives two possible solutions for the modulation of composition:

$$\text{(i)} \quad \tau_g \ll \tau_d (F \to 0), \quad A_0 + B_{nl}(\overline{\delta c_{\text{eq}}}) = 0 \tag{11}$$

and

$$\text{(ii)} \quad \tau_g \gg \tau_d (F \to 1), \quad [A_0 + B_{nl}(\overline{\delta c_{\text{eq}}})]\overline{\delta c_{\text{eq}}} = -A_0. \tag{12}$$

In the first case, (i), the existing modulated profile is adjusted by the atomic diffusion. The critical temperature for the modulation, T_c^M, is obtained by solving Eq. (11) and it is independent of the growth rate. This solution corresponds to the Malishkin model.[9] In the second case (ii), described by Eq. (12), the growth rate is so fast that the atomic diffusion does not allow the system to reach the kinetic equilibrium. The progression of the modulation depends on the amplitude of the initial modulation. The maximum critical temperature for this modulation, T_c^I, is described by the Ipatova model.[4] Therefore, it is necessary to determine which are the temperature ranges and the useful growth time for the different modulation expressions. The value of the function F determines the type of possible modulation and, therefore, it establishes the critical temperature for spinodal decomposition using a defined epitaxial growth rate.

Now we will apply the new formulation for the case of InGaAs epilayers. For InGaAs alloys we use $E_s = 1.4$ eV (Ref. 11) and $D_0 = 2.41$ cm^2/s as estimated from experimental data.[12] The experimental modulation wavelength, k_{II}, oscillates between 5 and 20 nm.[13–15] The choice of a value of 15 nm seems to be reasonable. In Fig. 1, the function F is represented for different growth times. At this stage, we define a new critical temperature, labeled critical transition temperature, $T_c^t(\tau_g)$, where $F(T_c^t, \tau_g) = 0.5$ for a given growth time. This critical temperature delimits two regions: (i) $T < T_c^t$, where only thermodynamic instability can generate modulation of composition[4] and (ii) $T > T_c^t$, where the diffusion can create kinetic instability that gives rise to modulation of composition.[9]

Figure 2 shows the new phase diagram of InGaAs alloys grown by epitaxial techniques using a typical growth rate of 0.1 ML/s. The critical temperatures delimit the modulated regions in the diagram. For $In_{0.5}Ga_{0.5}As$ alloys, the epilayers will be homogeneous above growth temperatures of $T_c^M = 1030$ K. Below this temperature, the alloy will present a kinetically stabilized composition modulation. However, the alloys again become homogeneous below a growth tempera-

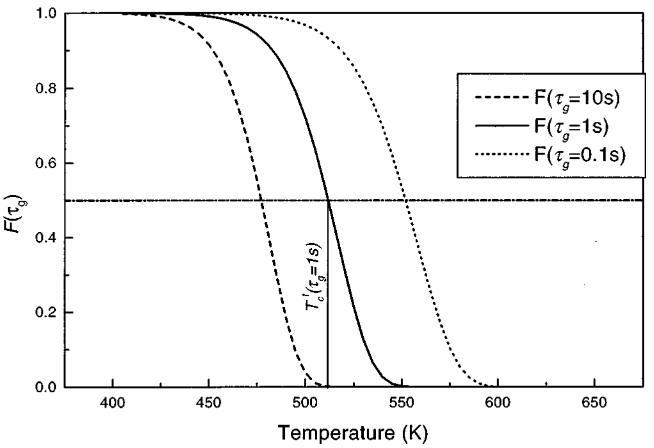

FIG. 1. The function F vs the growth temperature for three different growth times, τ_g. The function F shows a faster decay from unity to zero in a short range of temperatures.

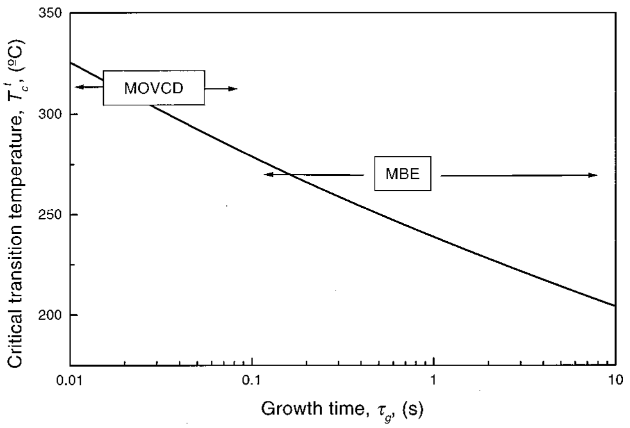

FIG. 3. The critical transition temperature, T_c^t, plotted vs the growth time, τ_g. The lower τ_g, the larger T_c^t. This causes a broader homogeneous window in the phase diagram.

ture of $T_c^t=523$ K. The composition modulation can appear again for inferior growth temperatures below $T_c^I=430$ K.

The dependence of T_c^t on the growth rate is shown in Fig. 3. The increase of the growth rate produces an enlargement of the homogeneity window between both regimes of composition modulation. Growth techniques like metalorganic chemical vapor deposition (MOCVD) need low growth temperatures around 300 °C to avoid the modulation in the layer. However, the usual growth temperatures in MOCVD are sensibly higher (>700 °C). In contrast, molecular beam epitaxy (MBE) uses lower substrate temperatures that minimize outdiffusion from the substrate and permit a precise growth rate control. In this technique, deposition times, τ_g, from 0.1 s to 10 s are used that correspond to T_c^t of 275 and 200 °C, respectively. Nevertheless, the difficulty to grow homogeneous layers with appropriate crystallinity by MBE at these temperatures is well known.[16] The use of techniques with lower growth temperatures (200–300 °C), such as ALMBE,[17] can allow the formation of homogeneous InGaAs alloys of any In content.

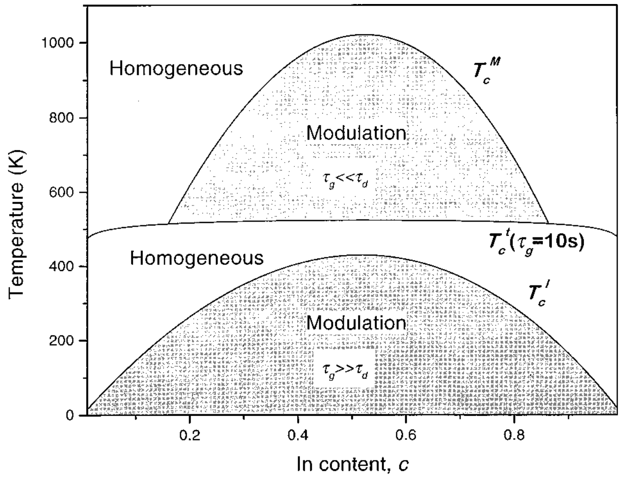

FIG. 2. Phase diagram of epitaxial InGaAs alloy for a growth time of 10 s. Two different regions of modulated alloys are separated by a homogeneous region due to the limitation of growth rate.

In conclusion, the influence of the growth temperature through superficial diffusion and of the deposition rate for different growth techniques on the modulation of composition is quantified. The existence of two different regimes of modulated composition is demonstrated and a phase diagram depending on the growth conditions is proposed. As a consequence, a window of homogeneity is defined inside the modulated composition regions in the proposed epitaxial phase diagram. The proposed model provides a different framework for epitaxial growths where temperature and growth rate regulation permit control of the modulation of composition in ternary and quaternary semiconductor alloys.

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