Control of phase modulation in InGaAs epilayers

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A theoretical description of the phase modulation state of epitaxial InGaAs layers has been recently published [D. González *et al.* Appl. Phys. Lett. **74**, 2649 (1999)]. To verify experimentally the deduced phase diagram, InGaAs structures with In compositional steps were grown using different growth conditions. Transmission electron microscopy studies have revealed the modulation state in each layer and have allowed us to define the experimental In composition and temperature dependence of the phase transition. The results show that InGaAs layers with and without composition modulation can be obtained by changing the growth temperature. An excellent agreement with the model predictions is observed. © *2000 American Institute of Physics.* [S0003-6951(00)05222-0]

A fundamental problem for the development of opto- and microelectronic devices is the control of their epilayer crystalline quality. Several factors can affect the achievement of perfect layers: first, the existence of a lattice misfit between the substrate and the epilayer can induce the formation of defects as misfit dislocations (MDs) and/or the appearance of a superficial roughness. Second, in the case of ternary or quaternary alloys, phenomena such as ordering or phase separation can occur[1,2] which also affect the optical and electrical properties of these structures. Therefore, control over both MD formation and phase modulation is necessary to achieve high device quality. One of the hindrances in the development of a predictive model is that these phenomena are dependent of each other. Indeed, the appearance of a superficial roughness can influence both MD formation[3,4] or phase separation.[5–7] Recently, the conditions of coupling between the surface morphology and the compositional modulation have been rigorously established theoretically.[8,9] The aim of this contribution is to confirm experimentally the previously published theoretical predictions[10] of the composition modulation (CM) state under different growth conditions.

Composition modulation in semiconductor epilayers has always been associated to the phenomenon of spinodal decomposition. From the first works of Springfellow[11] and Hénoc *et al.*[12] until the present time,[6,13] thermodynamic approaches have only been used and serious discrepancies between experimental and theoretical results remain [see Table I (Ref. 13)]. Recent studies,[14] introducing the effect of the kinetic instabilities in the epitaxial growth, have proposed a critical temperature of CM, T_c^M, able to explain to the CM observed in epilayers grown at typical substrate temperatures. This relative success was put in the shade by the predictions that no homogeneous layers below T_c^M can be obtained. This result implies that all the InGaAs epilayers with a lattice parameter close to the InP would present CM at typical growth temperatures used in molecular beam epitaxy (MBE) or metalorganic chemical vapor deposition (MOCVD).[4] The model we have recently published[10] diverges from this assumption and proposes a phase diagram where a window of homogeneous composition exists for low temperatures and growth rates. In the following, the equations used in the model are summarized.

The time evolution of the composition profile during an epitaxial growth can be described by:[14]

$$\frac{\partial \overline{\omega c}}{\partial t} = -\frac{k_{\mathrm{II}}^2 D^*}{T} A_0 \overline{\omega c} + \frac{k_{\mathrm{II}}^2 D^*}{T} [A_0 + B_{\mathrm{nl}}(\overline{\delta c}_{\mathrm{eq}})] \overline{\delta c}_{\mathrm{eq}}, \tag{1}$$

where $\overline{\omega c}$ is the deviation amplitude of the modulation profile in equilibrium, $\overline{\delta c}_{\mathrm{eq}}$, k_{II} is the CM wavelength and A_0 is defined as

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

where f is the free energy density and B_0 and B_{nl} are elastic energy functions related to the phase coherence. If the coefficients of this equation are independent of $\overline{\omega c}$, integration over a growth time, τ_g, defined as the necessary time to deposit one monolayer is

$$\overline{\omega c} = \left(1 + \frac{B_{\mathrm{nl}}(\overline{\delta c}_{\mathrm{eq}})}{A_0}\right) \overline{\delta c}_{\mathrm{eq}} + \exp\left(-\frac{\tau_g}{\tau_d}\right), \tag{3}$$

where, τ_d, is the diffusion time defined as the average time for adatom incorporation on the surface.

The second term of Eq. (3) is bounded between 0 and 1. The boundary condition for a stable CM is $\overline{\omega c} = 0$ and therefore, there are two limiting solutions:

$$\text{(i)} \quad \text{for } \tau_g \gg \tau_d, \quad A_0 + B_{\mathrm{nl}}(\overline{\delta c}_{\mathrm{eq}}) = 0, \tag{4}$$

and

$$\text{(ii)} \quad \text{for } \tau_g \ll \tau_d, \quad [A_0 + B_{\mathrm{nl}}(\overline{\delta c}_{\mathrm{eq}})] \overline{\delta c}_{\mathrm{eq}} = -A_0. \tag{5}$$

In case (i), the growth is so slow that the equilibrium profile is reached and the CM is governed by the kinetic instabilities. The critical temperature for the modulation, T_c^M, which depends on the growth rate, was defined by Malishkin *et al.*[14] as

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$$T_c^M = \frac{1}{2R\left(\frac{1}{1-c}+\frac{1}{c}\right)} \times\left[\Omega+(c_{11}+2c_{12})\frac{c_{11}-c_{12}}{c_{11}}\frac{c_{12}}{c_{11}+c_{12}}V\left(\frac{1}{a}\frac{\partial a}{\partial c}\right)^2\right], \quad (6)$$

where R is the gas constant, Ω the interaction parameter related to the mixed enthalpy, c_{ij} the elastic constants, V the molar volume, and a the lattice parameter of the solid solution.

In case (ii), the growth rate is so fast that only thermodynamical instability can occur and the CM progression depends on possible compositional fluctuation along the growth direction, z. Now two possible cases can be distinguished:

$$\text{(ii a)}\ \overline{\delta c}_{\text{eq}} \neq f(z), \quad A_0 = 0, \quad (7)$$

which correspond to the Springfellow solution[11] and

$$\text{(ii b)}\ \overline{\delta c}_{\text{eq}} \propto \exp[k_{\text{II}}(z-h)], \quad 2A_0 + B_{\text{nl}}(\overline{\delta c}_{\text{eq}}) = 0, \quad (8)$$

which coincides with the solution proposed by Ipatova *et al.*[13] In that case, CM occurs at temperatures below[13] T_c^{I}, where T_c^{I} is given by:

$$T_c^{\text{I}} = \frac{1}{2R\left(\frac{1}{1-c}+\frac{1}{c}\right)} \times\left[\Omega-\frac{(c_{11}+2c_{12})(c_{11}-c_{12})}{2(c_{11}+c_{12})}V\left(\frac{1}{a}\frac{\partial a}{\partial c}\right)^2\right]. \quad (9)$$

The physical phenomena that occur increasing temperature can be summarized as follows: at low temperatures thermodynamic instabilities govern, while kinetic instabilities are predominant at high temperatures. This means that at low T when $T<T_c^{\text{I}}$, CM occurs as a result of the thermodynamic equilibrium and this CM vanishes after crossing the T_c^{I} limit. Above T_c^{I}, τ_d continues diminishing and only when $\tau_g \approx \tau_d$, kinetic instabilities become important and the CM appears again. The transition from a thermodynamic to a kinetic mechanism is defined by the ''critical transition temperature,'' T_c^t, previously defined as[10]

$$T_c^t = \frac{E_s}{k\ln\left(\frac{\ln(0.5)}{k_{\text{II}}^2 D_0 \tau_g}\right)}, \quad (10)$$

where E_s is the activation energy of the superficial diffusion, k the Boltzmann constant, and D_0 the preexponential factor of the superficial diffusion coefficient.[15] This temperature depends fundamentally on the superficial diffusion and on the growth rate.

Defined by the critical transition temperatures the different modulation regimes, the InGaAs phase diagram obtained for a growth rate of 0.1 ML/s is shown in Fig. 1. At a growth temperature of 673 K, the model predicts homogeneous InGaAs layers occur for In contents below 22% and CM occurs for higher In content. The CM should increase with the In content, since the system moves away from the Malishkin limit condition, T_c^M, due to the progression of the kinetic instabilities. On the other hand, at 473 K, the InGaAs layers should be homogeneous over the whole composition range.

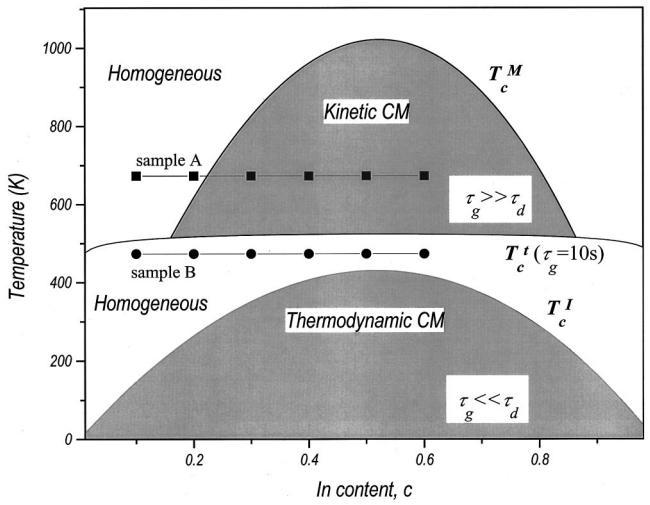

FIG. 1. Phase diagram of epitaxial InGaAs alloys for a growth time, $\tau_g = 10$ s. At 670 K the CM transition is predicted at 22% In content while at 473 K the layers remain homogeneous.

To improve the precision of the model, two sets of samples were grown. The samples consist of step-graded structures grown by the ALMBE technique[16] with a growth rate of 0.1 ML/s at two growth temperatures: 673 K (sample A) and 473 K followed with a thermal annealing of 7 min at 723 K (sample B). The increments of the In content are from 10% up to 60% and the layer thicknesses are 120 nm for $x=0.1$–0.4 and 80 nm for $x=0.5$–0.6. At the top, an InP layer of 500 nm has been grown to ensure a state of saturated

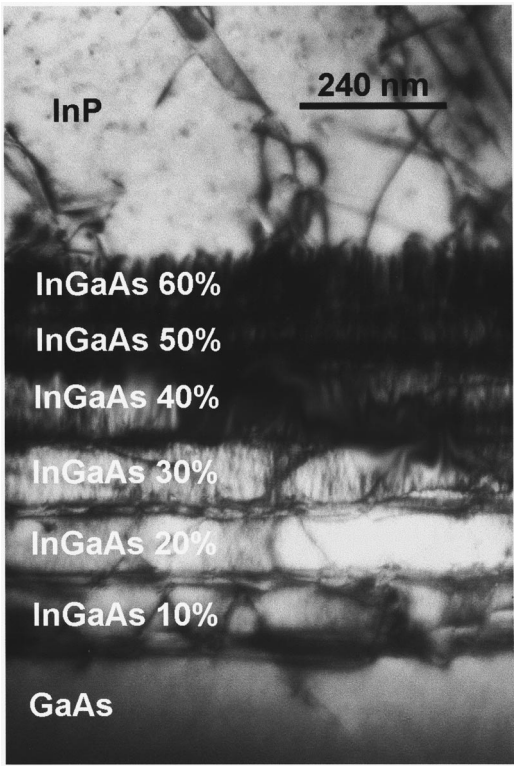

FIG. 2. XTEM micrograph of sample A using a 220 BF reflection. The $In_xGa_{1-x}As$ layers above $x=0.2$ show a clear and dark fringe pattern associated to a CM.

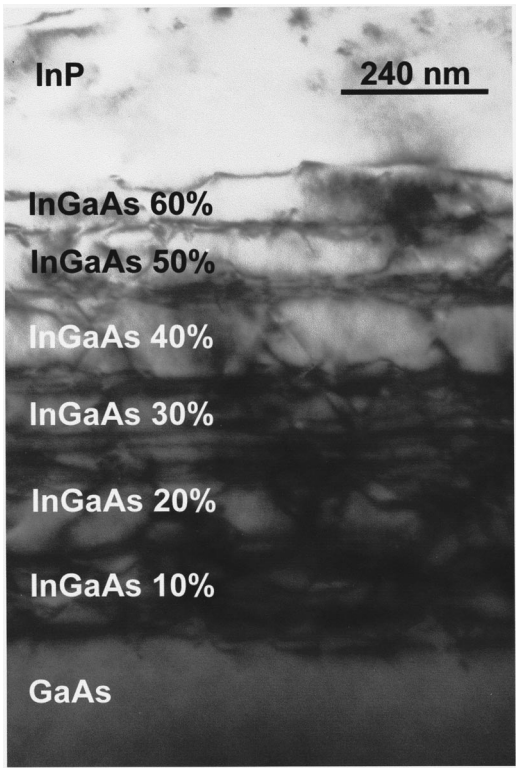

FIG. 3. XTEM micrograph of sample B using a 220 BF reflection. All of InGaAs layers show a homogeneous contrast without any CM.

relaxation, i.e., work hardening regime[17,18] in all the InGaAs layers. Step-graded structures were grown to avoid the influence on the CM of the different growth conditions involved with the misfit relaxation of single $In_xGa_{1-x}As/GaAs$ layers. Then each layer reaches the work-hardening regime during the growth showing no differences in the stress state and avoiding island growth[18] which does not mean avoiding surface roughing is observed. It results in a single sample where layers are grown in the similar conditions with similar defect distribution and relaxation state, but with different In contents.

To study the CM, cross sectional TEM (XTEM) has been used. Figure 2 shows an XTEM micrograph of sample A grown at a substrate temperature of 673 K. The InGaAs layers with an In content lower than 20% show homogeneous composition, but for higher compositions a typical structure of bright and dark fringes parallel to the growth direction is distinguished. This modulation disappears with the bright field (BF) 004 or weak beam (WB) 220 reflections indicating a typical CM behavior along the [110] directions in the growth plane.[19] The CM begins in the $In_{0.3}Ga_{0.7}As$ layer and increases with the In composition. The modulation wavelength, k_{II}, stays around 15 nm and is independent of the layer composition. On the other hand, the increase of the fringe contrast with the In composition is attributed to an increase of the modulation amplitude when the system moves away from the T_c^M that corresponds to the state of lowest modulation amplitude. The modulated InGaAs layers show wavy interfaces as predicted by Leonard *et al.*[20]

Figure 3 shows an XTEM micrograph of sample B. The CM behavior is totally different with respect to the previous structure. The contrast at the top layers is similar to that of the buried layers and no CM is observed at all. The growth mode, based on a slow growth rate at low temperature, eliminates phase separation in the high In content alloys and is in good agreement with our model predictions.

An important result that must be pointed out is the impact of CM on the defect distribution. The InP layer of sample A presents a high density (10^9 cm^{-2}) of threading dislocations (TD), behavior in contrast to sample B. In the latter, the TD density is determined by planar view TEM to be lower than 10^7 cm^{-2}. The elimination of the CM through the growth control improves the crystalline quality of the materials and therefore, the CM model predictions constitute a new tool in the device structures design.

In summary, a phase diagram applied to epitaxial InGaAs alloys is shown to describe with good accuracy, the transition temperatures between homogenous and CM states. Indeed, using step-graded structures to avoid differences in the growth conditions, the CM of the $In_xGa_{1-x}As$ layers ($0.1<x>0.6$) agrees well with the proposed phase diagram predictions. Growth at 473 K allows us to obtain homogeneous InGaAs layers with a better quality with respect to the generation of crystalline defects. This result constitutes evidence of the relationship between growth conditions (substrate temperature and growth rate) and the CM epitaxially grown structures.

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