INSTITUTE OF PHYSICS PUBLISHING SEMICONDUCTOR SCIENCE AND TECHNOLOGY

Semicond. Sci. Technol. **20** (2005) 1096–1102 doi:10.1088/0268-1242/20/10/019

An approach to the formation mechanism of the composition fluctuation in GaInNAs quantum wells

M Herrera[1], D González[1], J G Lozano[1], M Gutierrez[1], R García[1], M Hopkinson[2] and H Y Liu[2]

[1] Departamento de Ciencia de los Materiales e I. M. y Q. I., Universidad de Cádiz,
Apartado 40, 11510 Puerto Real, Cádiz, Spain
[2] Department of Electronic and Electric Engineering. University of Sheffield, Mappin Street,
Sheffield S1 3JD, UK

Received 24 May 2005, in final form 13 July 2005
Published 19 September 2005

Abstract

This work is focused on the study by transmission electron microscopy of the composition inhomogeneity of GaInNAs quantum wells. A variation of the contrast along the quantum well is reported which is related to phase separation in the alloy. This variation becomes more intense on increasing the growth temperature. From the intensity profiles taken from the images, we have calculated the energy of activation for surface diffusion in the alloy. The results suggest that the diffusion of indium controls the process of formation of phase separation. With regard to the thermodynamics of the process, we have extended the spinodal decomposition model of Ipatova to the quaternary alloy GaInNAs. Our calculations have shown that composition fluctuations of indium are stimulated by the introduction of nitrogen into the ternary alloy GaInAs. It is proposed that the observed compositional inhomogeneity of GaInNAs is composed mainly of a fluctuation of the indium content but secondly that N bonds preferentially to Ga-rich regions in the alloy.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Long-wavelength lasers emitting in the 1.3 to 1.6 μm range form the cornerstone of telecommunications optoelectronic devices. For this technological purpose, much work has been devoted in the last few years to the epitaxial growth and characterization of dilute nitrogen-containing GaInNAs quantum wells. The bandgap energy of GaInAs alloys can be reduced by a small N composition due to a large bandgap bowing of the III–V-dilute N compound [1]. This unusual behaviour is a consequence of the small size and high electronegativity of the N atoms. As a result, GaInNAs based light sources such as 1.3 μm wavelength lasers [2] and 1.45 μm wavelength light emitting diodes [3] have been demonstrated on GaAs substrates.

However, the dilute nitrides of III–V alloys have the disadvantage of the low solubility of N in these systems [4], inducing a large miscibility gap and making them difficult to grow with good homogeneity. The appearance of composition fluctuations in GaInNAs quantum wells has been reported [5] and this effect is known to be relatively easy to overcome by growing at low temperature [6], but the efficiency of light emission is degraded due to the presence of non-radiative defects in low growth temperature III–V materials [7] and these defects, arising mainly from poor stoichiometry, may only be partially removed by post-growth thermal processing. On the other hand, it should be noted that the problem of the phase separation in GaInNAs when introducing N is more complicated than expected, because it is a quaternary alloy and fluctuations in the group III and in the group V composition may be expected. The composition profile of each of the alloy constituents could influence the behaviour of the remaining species, stimulating or suppressing the intermixing. In this work, we report a study by transmission electron microscopy of the composition fluctuations of GaInNAs quantum wells with increasing growth temperature. Our purpose is to shed light on the mechanism of formation of the phase separation in this alloy, and to evaluate which alloy constituent (In or N) controls the composition profile.

2. Experimental details

Two sets of GaInNAs samples have been grown by molecular beam epitaxy (MBE) on (0 0 1) GaAs substrates in a VG V80H MBE system equipped with an Oxford Applied Research HD25 radio-frequency plasma source for N. The N flux was controlled by monitoring the intensity of the atomic N plasma emission with a photodiode. The nitrogen content in the epilayers was calibrated from the x-ray diffraction analysis of bulk samples and GaNAs quantum wells grown using similar plasma emission intensities. The first set of samples consists of four structures with $Ga_{0.62}In_{0.38}N_{0.023}As$ simple quantum wells 8 nm thick embedded between $GaAsN_{0.007}$ barrier layers with thickness 52 nm. The growth temperature of these samples is 360 °C, 400 °C, 440 °C and 460 °C, respectively. With regard to the second set of samples, the design of the structures is similar to the previous one, but with the difference that a 2 nm layer of intermediate composition $Ga_{0.88}In_{0.12}N_{0.019}As$ was inserted before and after each well, which we refer to as diffusion suppressing layer (DSL). This set of samples comprises five structures, grown at 375°, 385°, 400°, 410° and 420 °C, respectively.

Samples were prepared for transmission electron microscopy (TEM) by mechanical thinning followed by ion milling for cross section (XTEM) observation. The TEM study was performed using a JEOL 1200EX and JEOL 2011 transmission electron microscopes operating at 120 and 200 kV, respectively.

3. Results

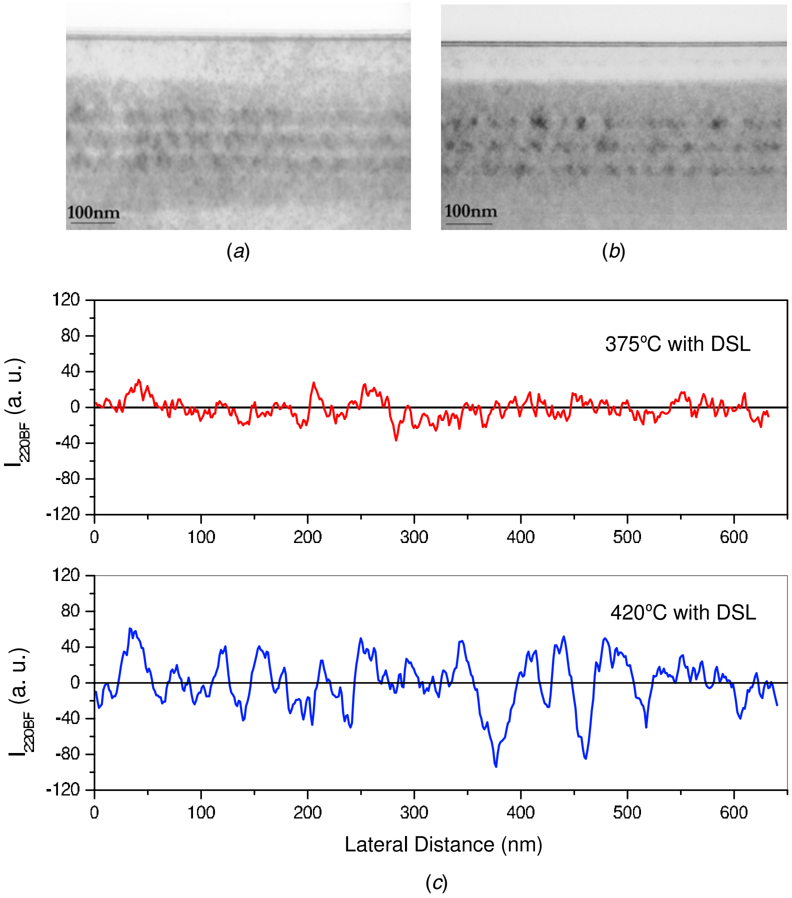
The TEM study of the structures with quantum wells grown at 360°, 400° and 440 °C has shown that these samples present good crystal quality, with planar morphology and without dislocations or other structural defects. When increasing the growth temperature to 460 °C, however, an undulation of the wells and the presence of threading dislocations are observed. Therefore it seems that the growth temperature is a key parameter to obtain high quality GaInNAs structures.

Despite the absence of structural defects in the samples grown at temperatures below 460 °C, observations of these structures by TEM using 220BF reflection (with $s = 0$ and close to the [1 1 0] pole to minimize the effect of thickness fluctuation) show the existence of dark and light strain contrasts with periodic character in all the wells, related to a phase separation in the alloy. The main feature observed in the present study is that these contrasts are more pronounced on increasing the growth temperature. In order to quantify the differences found between the samples grown at different temperatures, the intensity profiles of the 220BF images taken in the upper well of each sample have been considered. Figure 1 shows 220BF micrographs of the samples with DSLs grown at 375° and 420 °C, where the intensity profiles taken from the upper well of both micrographs and normalized with the GaAs substrate have been included. Figure 2 shows a summary of the results obtained with 220BF in the present work. In this figure, the average amplitude of the intensity profiles taken from 220BF images in the samples with simple quantum wells and in quantum well structures with DSLs is plotted versus the growth temperature. It should be noted that the amplitude of the strain contrasts in both sets of samples present a similar tendency with temperature; therefore the insertion of DSL seems not to affect drastically the lateral phase separation in the alloy. On the other hand, the GaInNAs samples considered have also been studied with compositionally sensitive 002DF reflection. In contrast to the results obtained with 220BF, this reflection does not show variations in the contrast along the wells in any of the samples, independent of the growth temperature and of the insertion of DSLs.

4. Discussion

The TEM results in diffraction contrast mode with the strain sensitive 220BF reflection have shown the existence of a periodic variation of the contrast along the quantum wells in the form of dark and light fringes in all the studied GaInNAs structures. For this reflection, variations in the contrast of an image appear mainly because of the existence of non-uniform elastic strain in the atomic planes of the material. However, we have not found structural defects that could be the origin of the non-uniform contrast in the wells. According to Vegards law, the lattice parameter of an alloy is a direct function of its composition in each region of the material. Hence, the modulation of the lattice parameter of the structure that causes the observed contrasts could be the result of the existence of a periodic phase separation in the alloy [7, 8]. Following this reasoning, our results have shown that the magnitude of the phase separation in the GaInNAs quantum wells is kinetically limited by the growth temperature.

It is well known that In modulation occurs in GaInAs structures (see review [9]) and also the existence of N modulation in GaAsN [8, 10, 11] has been observed. In the case of diluted nitrides GaInNAs, there are also some works about the Indium composition modulation [12–14]. The use of chemical contrast 002DF image analysis to observe In inhomogeneities for GaInAs compounds [15–17] and even for GaInNAs [5, 18, 19] is checked recently by many researchers. Thus, Albrecht *et al* [18] or Patriarche *et al* [19] have reported In-concentration fluctuations of 5–7% in a similar quaternary alloy using 002DF calibrations. Regarding the N sensitivity, if we use Bloch wave calculation [20], we should be able to detect differences of 0.5% of N for the same In content (relative intensities higher than 10%). The large difference between the atomic factor of N and of the other alloy constituents (Ga, In and As) explains this relatively high sensitivity. However, we think that it is possible to assess experimentally smaller differences in N content. The 002DF analysis could be more sensitive for N modulation because the inhomogeneity introduces a higher strain field that influences the contrast [21, 22]. In this sense, Suemune *et al* [23] have developed a 002DF study of GaNAs layers with nitrogen content of 2.8% (similar to our samples). Their 002DF images show quasi-periodic vertical dark stripe contrast with the stripe lying



(*a*) (*b*)

(*c*)

Figure 1. 220BF images of the samples with strain relief layers grown at 375 °C and 420 °C ((*a*) and (*c*), respectively), and intensity profiles (*b*) taken from the upper well in these images.

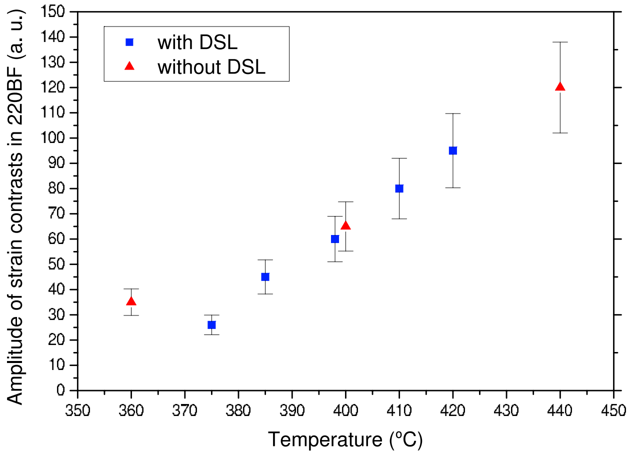


Figure 2. Plot of the amplitude of strain contrasts from the intensity profile taken in 220BF images of the studied samples versus the growth temperature.

perpendicular to the (0 0 1) growth plane that correspond to material with two different alloy compositions where the dark stripe corresponds to an As-rich phase and the bright contrast to an N rich phase.

The results mentioned above show the sensitivity of the 002DF analysis to detect In and N inhomogeneities in GaInNAs structures. In our case, periodic contrasts have not been found in any of the quantum wells studied with the composition-sensitive reflection 002DF. As discussed in more detail in a previous paper [24], the intensity of the 002DF reflection in the $Ga_{1-x}In_xN_yAs_{1-y}$ alloy can be expressed as

$$\begin{aligned} I_{002} &= C|F|^2 = 4C(f_{\mathrm{III}} - f_{\mathrm{V}})^2 \\ &= 4C[x f_{\mathrm{In}} + (1-x) f_{\mathrm{Ga}} - y f_{\mathrm{N}} - (1-y) f_{\mathrm{As}}]^2 \end{aligned}$$

where C is a factor that depends on thickness and imaging conditions, F is the structure factor and f are the atomic scattering factors. Because we are considering a quaternary alloy, infinite combinations of In and N contents can give place to the same intensity I_{002}. In an alloy with modulated composition, an increase in In and N content in a particular area (Δx and Δy, respectively) produces a decrease in the composition of these constituents in the same proportion in other regions, given that we are considering a closed system. Consequently, to obtain the same dark field intensity in two different regions of the material A and B, the condition

$$I^A_{002}(x + \Delta x, y + \Delta y) = I^B_{002}(x - \Delta x, y - \Delta y)$$

should be satisfied.

Solving this, we obtain

$$\Delta x = -\frac{f_{\mathrm{As}} - f_{\mathrm{N}}}{f_{\mathrm{In}} - f_{\mathrm{Ga}}}\Delta y = -2.208\Delta y.$$

Therefore, to observe a uniform contrast in the image of a GaInNAs quantum well with the 002DF reflection it is necessary that any increase in the N composition, Δy, is accompanied by a simultaneous decrease in the In content, Δx, in a proportion $\Delta x \approx -2.2\Delta y$. It is worth mentioning that this relation should be considered as an approximation to the composition profile in the alloy because of experimental errors in the measurements, as detailed in [24]. This result means that areas of the material rich in In should be poor in N, and vice versa. In other words, N prefers to bond Ga atoms than In ones. The local environment of N atoms in the GaInNAs alloy is determined by competition between chemical bonding and strain. During growth, chemical bonding governs the process occurring at the surface, favouring Ga–N bonds instead of In–N [25] because of the higher cohesive energy in GaN (2.24 eV versus 1.93 eV per bond, respectively) and inducing the composition profile found in the present work. Experimental evidence obtained by Fourier transform infrared absorption spectroscopy has been reported indicating that N only bonds to Ga atoms during the growth of GaInNAs [26, 27]. However, although the presence of In composition modulation is showed, the N distribution cannot be resolved up to now by nanoscale analytical techniques for these N content [12, 13]. Only STEM analyses of high N content GaInNAs single layers have shown that the microstructure is segregated resulting in an alloy containing GaIn(N)As and GaN-like phases [14], in good agreement with our experimental results. All these facts support the initial N and In separation that would explain the high strain fields observed with the 220BF and the absence of contrast modulation with the 002DF. Certainly, as demonstrated by Rubel [8] in bulk material, the most thermodynamically stable configuration is the formation of In-rich nitrogen clusters and, if nitrogen diffusion happens, this process should occur although the very low bulk diffusion coefficients ($\sim 10^{-13}$ cm^2 s^{-1}) limits the extension of this process even to high post-growth temperatures [28]. In the following, we evaluate the mechanism of formation of the phase separation in the GaInNAs alloy, both from the kinetics and the thermodynamics of the process.

4.1. Thermodynamics of the phase separation in GaInNAs

The prediction of composition modulation in semiconductor alloys has been widely made by means of spinodal decomposition models. Spinodal decomposition is a process of phase separation in which the atomic species diffuse spontaneously in the bulk driven by a reduction in the global free energy of the system. Although many studies have suggested that composition fluctuations in these alloys occurs by surface diffusion, the classical spinodal decomposition treatment continues to be a starting point to predict the thermodynamic tendency of different alloys (including GaInNAs [29, 30]) to suffer composition modulation. In relation to this, amongst the models found in the literature it is worth highlighting the one developed by Ipatova [31] because it considers that the composition fluctuations are formed in the surface of the structure, remaining frozen during the subsequent growth. Therefore, this would seem an appropriate starting point for our analysis.

Table 1. Values of enthalpy and entropy of formation of the binaries GaAs, InAs, GaN and InN, and interaction parameters between them, used in this work.

Binary	Enthalpy (10^3 J mol^{-1})	Entropy (J mol^{-1} × K)	Interaction parameter (10^4 J mol^{-1})
GaAs	−535 [51]	64.1 [52]	$\Omega_{\text{InN–GaN}} = 4.53$ [53]
InAs	−477 [53]	75.5 [54]	$\Omega_{\text{GaAs–GaN}} = 21.6$ [54]
GaN	−156.8 [55]	30.0 [56]	$\Omega_{\text{InAs–InN}} = 14.6$ [57]
InN	−28.6 [58]	31.6 [59]	$\Omega_{\text{InAs–GaAs}} = 1.89$ [57]

We extend the spinodal decomposition model proposed by Ipatova for ternary alloys to the quaternary GaInNAs with the purpose to study the influence of the introduction of N in the alloy on the composition fluctuations of In. For this calculation, the condition of the spinodal for quaternary alloys [32]

$$\frac{\partial^2 F(x,y)}{\partial x^2}\frac{\partial^2 F(x,y)}{\partial y^2} - \left(\frac{\partial^2 F(x,y)}{\partial x \partial y}\right)^2 = 0 \qquad (1)$$

is used, where F is the global free energy of the alloy, which is the sum of the chemical energy (F_{chem}) and the strain energy (F_{strain}).

In the regular solution approximation, the chemical energy of a quaternary system $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$ is calculated as [33]

$$\begin{aligned} F_{\text{chem}} = {} & xy\mu_{\text{InN}} + x(1-y)\mu_{\text{InAs}} + (1-x)y\mu_{\text{GaN}} \\ & + (1-x)(1-y)\mu_{\text{GaAs}} + x(1-x)y\Omega_{\text{InN–GaN}} \\ & + xy(1-y)\Omega_{\text{InAs–InN}} + x(1-x)(1-y)\Omega_{\text{InAs–GaAs}} \\ & + (1-x)y(1-y)\Omega_{\text{GaAs–GaN}} + W \end{aligned} \qquad (2)$$

where

$$\begin{aligned} W = {} & RT[xLn(x) + (1-x)Ln(1-x) \\ & + yLn(y) + (1-y)Ln(1-y)], \end{aligned} \qquad (3)$$

μ is the chemical potential of the pure binary compounds and Ω is the interaction parameter between the binaries. We have calculated the chemical potentials of the binaries AB from the values of entropy (S_{AB}), enthalpy (H_{AB}) and specific heat capacity at constant pressure $\left(C_p^{AB}\right)$ as [29]

$$\mu_{AB} = H_{AB} - TS_{AB} + \int_{298.15}^{T} C_p^{AB}\,\mathrm{d}T - T\int C_p^{AB}\,\mathrm{d}T/T \qquad (4)$$

Table 1 shows the values of S, H and Ω for the binaries in the GaInNAs alloy used in the calculation of the miscibility gap. The specific heat capacity at constant pressure has been taken from [34] and [35]. On the other hand, the expression for the elastic energy in the surface of the alloy proposed by Ipatova [31] is

$$F_{\text{strain}} = \frac{(c_{11} - c_{12})(c_{11} + 2c_{12})}{c_{11} + c_{12}}\varepsilon^2 \qquad (5)$$

where c_{11} and c_{12} are the elastic constants of the alloy and ε is the elastic strain. We have calculated these elastic constants for GaInNAs from the extrapolation of the corresponding to the binaries [36, 37].

Figure 3 shows the critical temperatures calculated as discussed above for the composition fluctuations of indium in GaInAs and GaInNAs. As shown in the figure, the critical temperatures for In in the quaternary alloy are much higher than in the ternary case. Group III composition fluctuations have been widely observed in the GaInAs alloy [38–40].

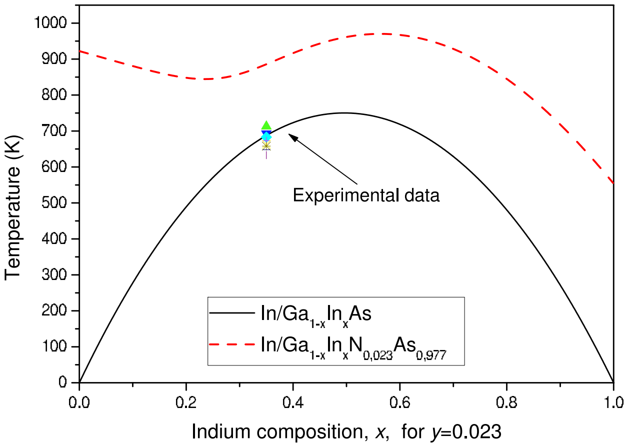


Figure 3. Spinodal decomposition curves for In in GaInAs (the full line) and GaInNAs (the dashed line) according to our extension of the model of Ipatova.

Higher critical temperatures for spinodal decomposition indicate a higher tendency for composition modulation in the alloy. This result is in accordance with the experimental data [24] and therefore these results show that the introduction of N in the alloy has a major influence on the phase separation of III adatoms. However, the precise spatial N distribution would be expected to have a further complicating effect on this phase separation. As we can see in table 1, GaAsN has a higher tendency to separate than InAsN and GaN is thermodynamically more stable than InN. These data would explain the tendency of N during the growth process (an open system) to move to Ga-rich regions according with our experimental results. However, in the bulk, the situation could be different. The high stress field profile associated with this distribution could be relaxed through the formation of phases rich in In–N bonds [8]. If diffusion is possible, induced either at the MBE growth temperature or during a post-growth annealing treatment, then N may migrate from Ga-rich regions to In-rich regions leading to a more homogeneous N distribution in the well. This behaviour could explain the blueshift in the photoluminescence response and the decrease in the contrast fluctuation in TEM images observed following the annealing process [41].

4.2. *Kinetics of the phase separation in GaInNAs*

Our experimental results with 220BF reflection have shown an increase in the intensity of the strain contrasts when raising the growth temperature, related to an increase in the magnitude of the composition fluctuations in the alloy. As shown above, the composition fluctuations in the alloy GaInNAs consist of alternate fringes due to regions enriched in In and N linked coherently. Changes in the growth temperature produce variations in the composition fluctuation of the two alloy constituents in a similar proportion, in such a way that although the magnitude of the fluctuations in both In and N increase with temperature, the relation $\Delta x \approx -2\Delta y$ should remain satisfied. Following this, a measurement of the variations in the intensity of the strain contrasts with temperature could constitute a good estimation of the evolution of the amplitude of the phase separation.

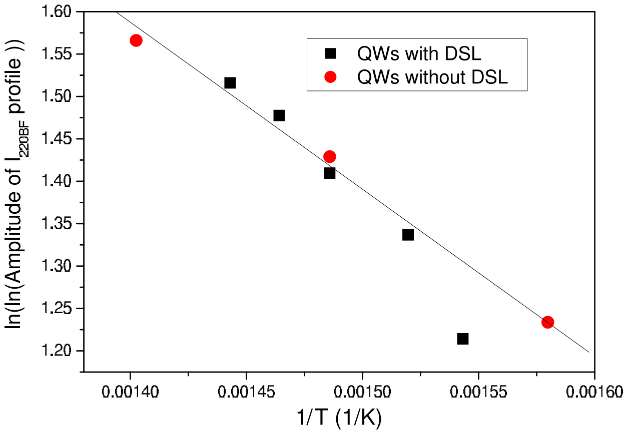


Figure 4. Double logarithm of the amplitude of strain contrasts measured in 220BF images versus the inverse of the growth temperature for the simple quantum wells and the wells with strain relief layers.

A relation between the amplitude of phase separation produced by diffusion and the temperature of the process has been previously proposed by Cahn [42]. The evolution with time t of the composition c of an alloy exhibiting a periodic phase separation can be described by

$$\frac{\partial c}{\partial t} = M\left\{\left(\frac{\partial^2 F}{\partial c^2}\right)\nabla^2 c\right\} + \text{non-linear terms} \qquad (6)$$

where M is the diffusion mobility and F is the free energy of the system.

This equation has a simple sine wave solution [43]

$$c - c_0 = \mathrm{e}^{R(\bar{\beta}t)}\cos\bar{\beta}\bar{r} \qquad (7)$$

where $R(\bar{\beta})$ is obtained by substituting this solution back into the diffusion equation, as

$$R(\bar{\beta}) = -M\beta^2\left(\frac{\partial^2 f}{\partial c^2}\right). \qquad (8)$$

The mobility M can be expressed as a function of the growth temperature as [43]

$$M = M_0\,\mathrm{e}^{-Q/RT} \qquad (9)$$

where Q is the activation energy of the diffusion process and M_0 is the pre-exponential factor.

According to these equations, the amplitude in the composition profile is related to the growth temperature by

$$c - c_0 \propto \mathrm{e}^{\mathrm{e}^{-Q/RT}}. \qquad (10)$$

Figure 4 shows a plot of the double logarithm of the amplitude of the intensity profile taken from 220BF micrographs versus the inverse of the absolute growth temperature for the GaInNAs quantum wells with and without strain relief layers. A linear fit of this data is also included. From the slope of these graphs, we have obtained an activation energy for adatom diffusion in GaInNAs of 0.19 ± 0.04 eV. In the literature, a value of 0.35 eV has been reported for the activation energy of In surface diffusion on (0 0 1) GaAs with A (2 × 4) surface reconstruction, 0.25 eV for (1 1 1)A and 0.29 eV for (1 1 1)B [44]. There have also been published values of 0.22 eV for the diffusion of In in InAs quantum dots [45] and 0.13 eV and 0.29 eV for the diffusion of In on $Ga_{0.33}In_{0.66}As$(0 0 1)−2 × 3 for the directions [1 $\bar{1}$ 0] and [1 1 0], respectively [60]. In the present work, we have not found differences between the ⟨1 1 0⟩ directions, although an asymmetry could exist within the experimental errors of the measurements. As can be observed, the energy of activation for GaInNAs structures calculated in this work is of the same order of magnitude as the values found in the literature for In in Ga(In)As alloys. Moreover, it should be mentioned that the quantum well studied contains 38% In but only 2.3% N. Therefore the behaviour of In is expected to have a much greater effect on the microstructure of the GaInNAs quantum wells than that of N. On the other hand, the existence of the same proportion between the composition fluctuations of In and N, independent of the growth temperature (as observed with 002DF reflection), indicates that the kinetics of the composition profile could be controlled just by one of the alloy constituents, with the second one becoming adapted to it. We have not found in the literature diffusion data for N in GaIn(N)As to be compared with our experimental results, but the obtained values suggest that it is the surface diffusion of In atoms that controls the phase separation in the GaInNAs alloy.

With regard to the samples with the quantum wells sandwiched between DSLs, it should be mentioned that this design has been proposed to improve the luminescence properties of this alloy [46–48]. In relation to the structural changes that these layers induce in the system, Peng *et al* [49] have suggested that the introduction of DSL reduces drastically the diffusion of In and N along the growth direction (out of the quantum well). However no indications of structural changes inside the quantum wells have been reported. Our study has shown that the composition fluctuations of GaInNAs quantum wells are not significantly affected by the introduction of $Ga_{0.88}In_{0.12}N_{0.019}As$ DSLs. The use of DSLs is therefore not expected to cause important local changes in the layer composition during growth and therefore the diffusion process inside layers should not be affected. This would explain the similarities in the results of composition fluctuations for structures with and without DSLs.

According to the experimental and theoretical results obtained in the present work, we can describe the mechanism of formation of the phase separation in GaInNAs as follows. Due to the higher concentration of In with regard to N in the GaInNAs structures studied (more than one order of magnitude higher) and according to the experimental values of activation energy for surface diffusion obtained in the present work, it is likely that the composition profile found experimentally is determined firstly by In atoms. During the MBE process, group III atoms are expected to suffer phase separation into Ga-rich and In-rich regions at the growing surface. In the GaInNAs alloy, these composition fluctuations are further stimulated with regard to the ternary alloy GaInAs because of the introduction of N in the alloy. While this composition profile is being developed, N atoms are attracted preferably towards the Ga-rich areas, clustering in these regions. This produces an independent composition profile for N. The resulting compositional profile presents an out of phase periodic enrichment in In and N in the alloy. However, this grown-in distribution can partially reverse through diffusion either at the MBE growth temperature or by post-growth annealing. This diffusion is favoured by the strain energy decrease, which accompanies the formation of N–In bonds in the GaAs host crystal. Recently, Uno *et al* [50] using fluorescence extended x-ray absorption fine structure (EXAFS) spectroscopy have shown that the number of In–N bonds in the GaInNAs crystal increases due to the diffusive driving force induced by thermal annealing. Further investigation is needed to know the degree of this diffusion process and the final distribution, which might be obtained due to optimal thermal annealing. Further work is also required to quantify the effect of this compositional inhomogeneity on the photoluminescence characteristics in order to result in optimal quantum wells required by optical device industries.

5. Conclusion

We have studied the composition profile and the mechanism of formation of the composition fluctuations in GaInNAs quantum wells with and without DSL. We have observed strain contrasts in all the quantum wells with 220BF reflection associated with composition fluctuations which are more pronounced on increasing the growth temperature. In contrast to these observations, micrographs obtained with 002DF reflection do not show periodic contrasts. These results indicate that there may exist two independent composition profiles for In and N, which are out of phase. To understand this behaviour, we have extended the spinodal decomposition model of Ipatova to the quaternary alloy GaInNAs, and these calculations have shown that the introduction of N in the GaInAs alloy stimulates the composition modulation of In with regard to its behaviour in the ternary alloy. From the amplitude of the strain contrasts, we have made an estimation of the activation energy for surface diffusion in GaInNAs of 0.19 ± 0.04 eV, which is a value similar to that corresponding to In in Ga(In)As. Our study suggests that In atoms could determine the initial composition profile in the alloy during growth, and that N atoms could then bond Ga-rich areas of the material.

Acknowledgments

Financial support from EPSRC (UK), CICYT project MAT2001-3362 and MAT2004-01234 (Spain) and the Spanish ministry of Education is gratefully acknowledged.

References

[1] Kondow M, Uomi K, Niwa A, Kitatani T, Watahiki S and Yazawa Y 1996 *Japan. J. Appl. Phys.* **35** 1273
[2] Kondow M, Kitatani T, Nakatsuka S, Larson M, Nakahara K, Yazawa Y, Okai M and Uomi K 1997 *IEEE J. Sel. Top. Quantum Electron.* **3** 719
[3] Sato S, Osawa Y and Saitoh T 1997 *Japan. J. Appl. Phys.* **36** 2671
[4] Ho I and Stringfellow G B 1997 *J. Cryst. Growth* **178** 1
[5] Grillo V, Albrecht M, Remmele T, Strunk H P, Egorov A Yu and Riechert H 2001 *J. Appl. Phys.* **90** 3792
[6] Bi W G and Tu C W 1997 *Appl. Phys. Lett.* **70** 1608
[7] Herrera M, González D, Hopkinson M, Navaretti P, Gutierrez M, Liu H Y and García R 2004 *Semicond. Sci. Technol.* **19** 813
[8] Rubel O, Volz K, Torunski T, Baranovskii S D, Grosse F and Stolz W 2004 *Appl. Phys. Lett.* **85** 13

[9] Zunger A and Mahajan S 1994 *Handbook on Semiconductors* vol 3 (Amsterdam/New York: Elsevier/North-Holland) pp 1399–512

[10] Goldman R S, Feenstra R M, Briner B G, O'Steen M L and Hauenstein R J 1996 *Appl. Phys. Lett.* **69** 3698

[11] Grenouillet L, Bru-Chevallier C, Guillot G, Gilet P, Ballet P, Duvaut P, Rolland G and Million A 2002 *J.Appl. Phys.* **91** 5902

[12] Gass M H, Papworth A J, Bullough T J and Chalker P R 2004 *Ultramicroscopy* **101** 257

[13] Chalker P R, Davock H, Thomas S, Joyce T B, Bullough T J, Potter R J and Balkan N 2001 *J. Cryst. Growth* **233** 1

[14] Bullough T J, Davies S, Thomas S, Joyce T B and Chalker P R 2003 *Solid-State Electron.* **47** 407

[15] Dorin C, Mirecki Millunchick J and Wauchope C 2002 *Appl. Phys. Lett.* **81** 3368

[16] Salviati G, Ferrari C, Lazzarini L, Nasi L, Drigo A V, Berti M, De Salvador D, Natali M and Mazzer M 2002 *Appl. Surf. Sci.* **188** 36

[17] Chin A and Chen W J 1996 *Appl. Phys. Lett.* **69** 443

[18] Albrecht M, Grillo V, Remmele T, Strunk H P, Egorov A Yu, Dumitras Gh, Riechert H, Kaschner A, Heitz R and Hoffmann A 2002 *Appl. Phys. Lett.* **81** 2719

[19] Patriarche G, Largeau L, Harmand J-C and Gollub D 2004 *Appl. Phys. Lett.* **84** 204

[20] Volz K, Torunski T and Stolz W 2005 *J. Appl. Phys.* **97** 014306

[21] Cagnon J, Buffat P A, Stadelmann P A and Leifer K 2001 *Inst. Phys. Conf. Ser.* **169** 31

[22] Glas F 2003 *Inst. Phys. Conf. Ser.* **180** 191

[23] Suemune I, Morooka N, Uesugi K, Ok Y-W and Seong T-Y 2000 *J. Cryst. Growth* **221** 546

[24] Herrera M, González D, Hopkinson M, Gutiérrez M, Navaretti P, Liu H Y and García R 2005 *J. Appl. Phys.* **97** 73705

[25] Matsuoka T, Sasaki T and Katsui A 1990 *Optoelectron. Devices Technol.* **5** 53

[26] Kurtz S, Webb J, Gedvilas L, Friedman D, Geisz J, Olson J, King R, Joslin D and Karam N 2001 *Appl. Phys. Lett.* **78** 748

[27] Alt H Ch, Egorov A Yu, Riechert H, Meyer J D and Wiedemann B 2001 *Physica B* **308–310** 877

[28] Stolwijk N A, Bosker G, Andersson T G and Sodervall U 2003 *Physica B* **340–342** 367

[29] Asomoza R, Elyukhin V A and Peña-Sierra R 2002 *Appl. Phys. Lett.* **81** 1785

[30] Schlenker D, Miyamoto T, Chen Z, Kawaguchi M, Kondo T, Gouardes E, Gemmer J, Gemmer C, Koyama F and Iga K 2000 *Japan. J. Appl. Phys.* **39** 5751

[31] Ipatova I P, Malyshkin V G and Shchukin V A 1993 *J. Appl. Phys.* **74** 7198

[32] de Cremoux B 1982 *J. Physique* **12** C5–C19

[33] Putnis A 1992 *Introduction to Mineral Sciences* (Cambridge: Cambridge University Press)

[34] Barin I, Knackeand O and Kubaschewski O 1977 *Thermochemical Properties of Inorganic Substances* (Berlin: Springer)

[35] Blakemore J S 1982 *J. Appl. Phys.* **53** R123

[36] Coleman J J 1993 *Quantum Well Lasers* (San Diego: Academic) 367

[37] Kim K, Lambrecht W R L and Segall B 1997 *Phys. Rev.* B **56** 7018

[38] Peiró F, Cornet A, Morante J R, Clark S A and Williams R H 1991 *Appl. Phys. Lett.* **59** 1957

[39] Okada T, Weatherly G C and McComb D W 1997 *J. Appl. Phys.* **81** 2185

[40] Lee K, Mahajan S and Johnson W C 1994 *Mater. Sci. Eng.* B **28** 209

[41] Patriarche G, Largeau L, Harmand J C and Gollub D 2004 *Appl. Phys. Lett.* **84** 203

[42] Cahn J W 1968 *Trans. Metall. Soc. AIME* **242** 166

[43] Cahn J W 1961 *Acta Metall.* **9** 795

[44] Matthai C C and Moran G A 1998 *Appl. Surf. Sci.* **123–124** 653

[45] Shiramine K, Itoh T, Muto S, Kozaki T and Sato S 2002 *J. Cryst. Growth* **242** 332

[46] Fedorenko Y, Jouhti T, Pavelescu E-M, Karirinne S, Kontinnen J and Pessa M 2003 *Thin Solid Films* **440** 195

[47] Bian L F, Jiang D S, Lu S L, Huang J S, Chang K, Li L H and Harmand J C 2003 *J. Cryst. Growth* **250** 339

[48] Li L H, Patriarche G, Lemaitre A, Largeau L, Travers L and Harmand J C 2003 *J. Cryst. Growth* **251** 403

[49] Peng C S, Pavelescu E M, Jouhti T and Pessa M 2003 *Solid-State Electron.* **47** 431

[50] Unoa K, Yamadaa M, Tanakaa I, Ohtsukia O and Takizawa T 2005 *J. Cryst. Growth* **278** 214

[51] 1978 *CRC Handbook of Chemistry and Physics* (Boca Raton, FL: CRC Press)

[52] Yamaguchi K, Chiba Y, Yoshizawa M and Kameda K 1996 *J. Japan. Inst. Metall.* **60** 1181

[53] Elyukhin V A and Nikishin S A 1996 *Semicond. Sci. Technol.* **11** 917

[54] Qiu Y, Nikishin S A, Temkin H, Elyukhin V A and Kudriavtsev Yu A 1997 *Appl. Phys. Lett.* **70** 2831

[55] Ranade M R, Tessier F, Navrotsky A, Leppert V J, Risbud S H, DiSalvo F J and Balkas C M 2000 *J. Phys. Chem.* B **104** 4060

[56] Unland J, Onderka B, Davydov A and Schmid-Fetzer R 2003 *J. Cryst. Growth* **256** 33

[57] Alt H Ch, Egorov A Yu, Riechert H, Meyer J D and Wiedemann B 2001 *Physica B* **308–310** 877

[58] Ranade M R, Tessier F, Navrotsky A and Marchand R 2001 *J. Matall. Res.* **16** 2824

[59] Onderka B, Unland J and Schmid-Fetzer R 2002 *J. Mater. Res.* **17** 3065

[60] Kratzer P, Penev E and Scheffler M 2003 *Appl. Surf. Sci.* **216** 436