INSTITUTE OF PHYSICS PUBLISHING SEMICONDUCTOR SCIENCE AND TECHNOLOGY

Semicond. Sci. Technol. **19** (2004) 813–818 PII: S0268-1242(04)74892-0

Influence of growth temperature on the structural and optical quality of GaInNAs/GaAs multi-quantum wells

M Herrera[1], D González[1], M Hopkinson[2], P Navaretti[2], M Gutiérrez[2], H Y Liu[2] and R García[1]

[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 Electrical Engineering, University of Sheffield, Mapping Street, Sheffield S1 3JD, UK

Received 20 January 2004
Published 18 May 2004
Online at stacks.iop.org/SST/19/813
DOI: 10.1088/0268-1242/19/7/005

Abstract

This work focuses on the influence of the growth temperature on the structural and optical quality of GaInNAs/GaAs and GaInAs/GaAs multi-quantum wells with similar lattice mismatch, studied by transmission electron microscopy and photoluminescence. We have found compositional fluctuations in all the GaInNAs samples, which vary from negligible to very strong over the temperature range studied (360–460 °C). In comparison, at the same growth temperature, GaInAs heterostructures appear more homogeneous. It is proposed therefore that the introduction of N in the structure could be responsible for the enhanced phase separation.

A broadening of the photoluminescence peak in GaInNAs structures when raising the growth temperature has also been found associated with the increase in composition fluctuations. Moreover, a kinetically limited Stranski–Krastanow growth mode has been observed in both GaInAs and GaInNAs structures, taking place at lower temperature in GaInNAs quantum wells. We suggest that the enhancement of this growth mode is a consequence of the increased phase separation. The influence of the introduction of N into the GaInAs alloy on the compositional fluctuations and 3D growth mode is discussed.

1. Introduction

Semiconductor lasers emitting at 1.3 and 1.55 μm wavelengths are essential light sources in optical networks due to their operation within the minimum loss and dispersion wavebands in optical fibre communications. The conventional GaInAsP/InP-based material used for these applications has the disadvantages of a high threshold current and a low characteristic temperature due to poor electron confinement [1], which makes the use of thermoelectric cooling indispensable. During the last decade, the dilute nitride–arsenide semiconductor GaInNAs was intensively investigated [2, 3] as a suitable candidate to overcome these inconveniences and to provide the additional advantages of established GaAs device technology, such as lower substrate cost, ease of fabrication and the advantageous refractive index properties of the AlGaAs ternary alloy. GaInAsN shows an extremely large negative band gap bowing [4] that allows a redshift of the emission wavelength by the incorporation of relatively low (<5%) N content in GaInAs structures. Moreover, it can be grown pseudomorphically on GaAs substrates with a type-I band line-up. Recently, GaInNAs/GaAs heterostructures have been applied to transverse lasers [5–7], vertical cavity surface emitting lasers (VCSELS) [8] as well as solar cells [9] and heterobipolar transistors [10].

In spite of the rapid pace of progress in the development of III–V dilute nitrides, research in this field is not still mature. High nitrogen contents have shown to degrade the optical quality of the films [11] due to N-related defects. Therefore, typical laser results are reported for devices with a nitrogen

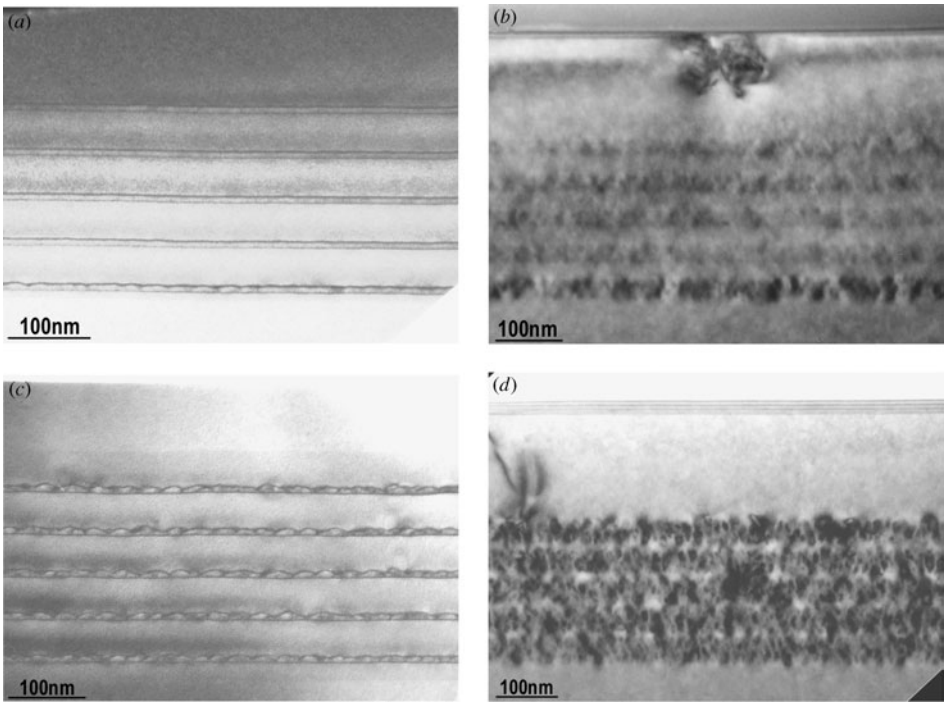


Figure 1. TEM micrographs of the structures grown at 400 °C (*a*) and (*b*) and 460 °C (*c*) and (*d*) obtained with 002DF reflection (*a*) and (*c*) and 220BF reflection (*b*) and (*d*).

content of around 1% and the In concentration is maximized [11–13]. However, these indium compositions are known to be within the miscibility gap of the GaInAs alloy and, as a consequence, are likely to be prone to phase separation, leading to localization effects in the photoluminescence (PL) such as the characteristic S-shape temperature dependence and an asymmetric peak shape. The phase separation problem has been partially overcome by growing GaInNAs at low temperature [14], but the efficiency of light emission is degraded due to the presence of non-stoichiometric defects [15], being partially recovered by annealing. Although it is known that the photoluminescence is very sensitive to the growth temperature [16], the origin of this dependence is still uncertain. The purpose of this paper is to investigate the influence of the growth temperature on the microstructure of GaInNAs/GaAs and GaInAs/GaAs multi-quantum wells and to compare these results with photoluminescence data.

2. Experimental details

GaInAsN heteroepitaxial growth was carried out in a VG V80H molecular beam epitaxy (MBE) system equipped with an Oxford Applied Research HD25 radio frequency plasma source for N. The N composition was controlled by monitoring the intensity of the N plasma emission and calibrated from the x-ray diffraction analysis of bulk samples grown under similar conditions. A set of samples with three GaInAsN quantum wells (QWs) embedded between 52 nm thick $GaAsN_{0.007}$ barriers were grown on (001) on-axis GaAs substrates. The wells have a nominal thickness of 8 nm and a nominal concentration $x = 0.38$ of In and $y = 0.023$ of N. The GaInNAs quantum wells were grown at different temperatures in each sample: 360 °C, 400 °C, 440 °C and 460 °C. For comparison, GaInAs QWs 8 nm thick with a nominal In content of $x = 0.3$ were also grown at two different temperatures: 460 °C and 515 °C.

Samples were prepared for transmission electron microscopy (TEM) by mechanical thinning followed by ion-milling for cross-section observation (XTEM). The TEM study was performed using a JEOL 1200EX transmission electron microscope operating at 120 kV, using mainly the 220BF and 002DF reflections. The structures were also studied by photoluminescence using Ar^+ ion excitation and a monochromator equipped with a GaInAs array detector.

3. Results

TEM results for the sample grown at the lowest temperature in our study (360 °C) exhibit no dislocations or any other structural defect. The 002DF reflection shows perfectly flat wells. However, very slight stress contrasts are observed in all the wells with 220BF reflection. On increasing the growth temperature to 400 °C, the quantum wells remain flat, as observed in figure 1(*a*), but the stress contrasts found with 220BF reflection are more pronounced, as shown in figure 1(*b*). Cross-section images of the GaInNAs sample grown at 440 °C demonstrate that when raising the growth temperature from 400 °C to 440 °C, the surface of the wells still remains flat. Moreover, the stress contrasts revealed with 220BF reflection are stronger than in the previous structures. Again, the first well exhibits a particular behaviour, showing some undulations. In addition, a few dislocations coming just from the first well have been observed. Finally, the sample grown at the highest temperature considered in this work, 460 °C, shows perfectly marked undulations in all the wells, of period approximately 20 nm (figure 1(*c*)). Moreover, the stress contrasts exposed with 220BF reflection are even more pronounced than in the other structures, as can be clearly seen

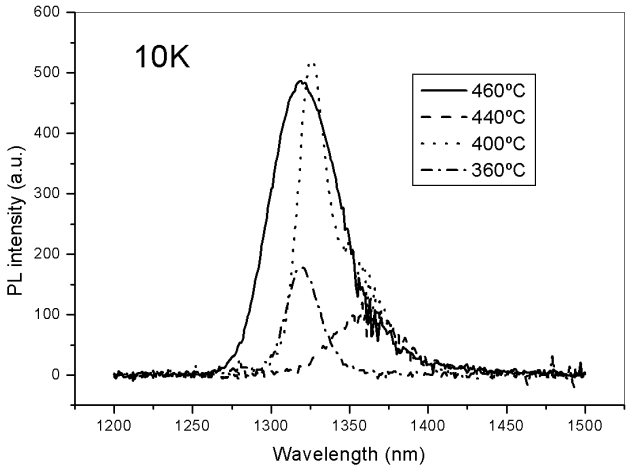
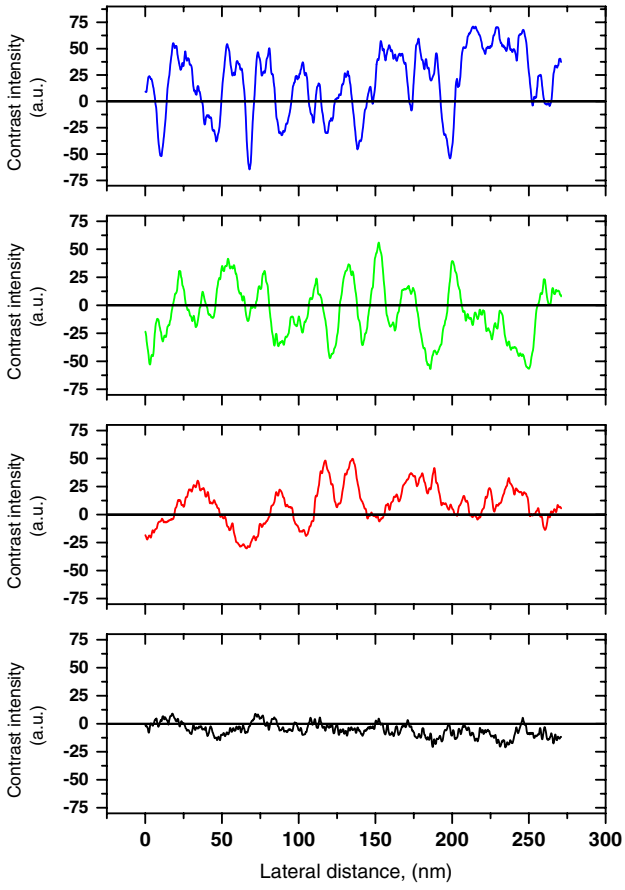


Figure 2. Low-temperature PL spectra of the GaInNAs structures.

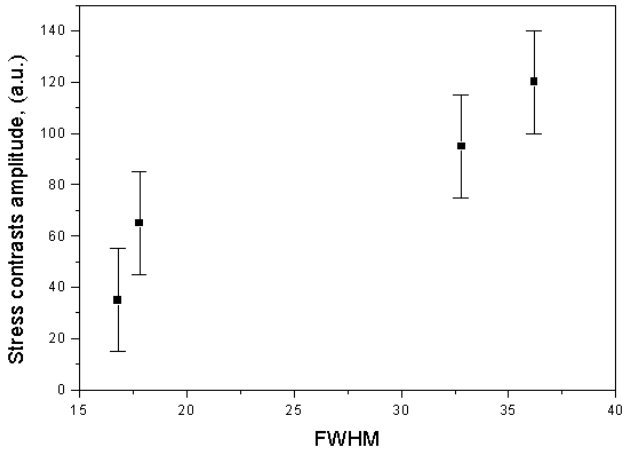
in figure 1(*d*). Some threading dislocations gliding towards the sample surface from all the wells also appear in this sample.

Figure 2 reveals the low-temperature photoluminescence characteristics of the above-described structures. The samples grown at 360 °C and 400 °C show narrow peaks at wavelengths close to 1.3 μm. The sample grown at 440 °C shows a broad low-intensity peak at a wavelength which coincides with that of the shoulder of the peak in the previous structure. It is possible that this PL comes from the first well and that the PL from subsequent wells is significantly reduced due to the presence of threading dislocations coming from this first well observed by TEM. Finally, the sample grown at 460 °C exhibits a high-intensity peak, broader than that corresponding to the previous structures. To correlate the broadening of the PL peak with the structural properties of these samples, diffraction contrasts intensity profiles from the upper well in the 220BF TEM micrographs in all the structures were collected (figure 3(*a*)). As expected, it has been observed that the tip height variations are higher when increasing the growth temperature of the samples. Moreover, the periodicity of the contrasts is reduced when raising the growth temperature. The average height variation versus the full width at half maximum (FWHM) in the PL peak is plotted in figure 3(*b*). It is clearly seen that the degradation of the optical properties is directly related to the features observed by TEM, given that the higher the height variation in the intensity profile, the wider the PL peak.

In order to separate the contribution of the In and the N atoms to the structural features found in these samples, quantum wells of the ternary alloy GaInAs were grown at different temperatures. The composition of these samples was chosen in such a way that the lattice mismatch is similar to that in the GaInNAs structures described above. 220BF micrographs of the $Ga_{0.7}In_{0.3}As$ structure grown at 460 °C show very slight stress contrasts. Also, the 002DF reflection shows that the well is perfectly flat. This is in contrast to the GaInNAs sample grown at the same temperature, which shows stronger stress contrasts and is undulated. On increasing the growth temperature until 515 °C, the $Ga_{0.7}In_{0.3}As$ QW is undulated, as can be observed in figure 4. Thus, both alloys GaInAs and GaInNAs, show the same behaviour with regard



(*a*)



(*b*)

Figure 3. (*a*) 220BF diffraction contrasts intensity profiles from the upper well in the GaInNAs samples. (*b*) Plot of amplitude of stress contrasts versus full width at half maximum (FWHM) in the PL spectra.

to the 3D growth mode, but in GaInAsN this takes place at a significantly lower temperature.

4. Discussion

4.1. Composition fluctuations

To clarify the origin of the contrasts observed with the stress-sensitive 220BF reflection in our samples we need to consider

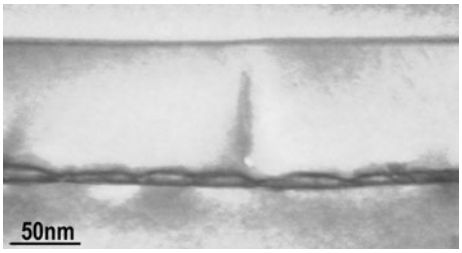


Figure 4. Cross-sectional image taken with 002DF of the GaInAs sample grown at 515 °C.

electron scattering in a deformed crystal, a phenomenon that is treated by means of the dynamical theory of diffraction contrast. Thus, the intensity of the incident and scattered waves is related to the displacement field ($R(r)$) of the atoms in a non-perfect crystal [17]. The variation in intensity of the electron beams gives rise to the contrasts observed in TEM images. The displacement field $R(r)$ can be produced by lattice defects such as dislocations as well as by the distortion of the atomic planes of a coherent thin layer. In our samples, the lattice mismatch between the GaInNAs quantum wells and the substrate is identical for the four structures, given that they all have the same composition. Therefore, in the absence of lattice defects, similar contrasts are expected. However, we have observed in our study that the contrasts are stronger on increasing the growth temperature of the quantum well, despite the fact that all the samples have the same composition. Moreover, although the structure obtained at 460 °C shows 3D growth, the other samples do not exhibit any structural defect at our resolution level that could be responsible for such contrasts. Therefore, the cause of the displacement field responsible for the contrasts observed with 220BF reflection needs to be examined as atomic plane distortion in the ⟨110⟩ directions. According to Vegard's law, the lattice parameter of any material system is directly related to its composition. Consequently, variations of composition inside a particular alloy would result in a modulation of its lattice parameter and hence in the apparition of a displacement field in the atomic planes. We believe that the origin of the contrasts observed with 220BF reflection is due to cation composition fluctuations in the wells as a consequence of In/Ga interdiffusion at increasing growth temperature. It is possible that there could be equivalent intermixing on the anion site, but the low N composition makes such effects difficult to resolve. In comparison, the GaInAs structure grown at 460 °C and with the same lattice mismatch than the GaInNAs samples shows only very slight contrasts with 220BF reflection. This means than the enhanced phase separation observed in GaInNAs wells is mainly due to the introduction of N in the GaInAs alloy.

It should be mentioned that, although our reasoning about the existence of composition fluctuations is based on the stress-sensitive 220BF reflection, the 002DF reflection is usually considered as a 'composition-sensitive' reflection. The 002DF reflection is associated with composition because its intensity depends on the difference in the atomic structure factors of the constituent atoms, whereas in 220BF it depends on the sum of these factors. In our case, we have not observed periodic contrasts with the 002DF reflection in any of the samples studied, which suggests that the magnitude of the phase separation is very low. The 002DF reflection is a relatively sensitive measure of compositional changes. We have observed diffraction contrast from GaAsNx/GaAs quantum wells of $x = 0.01$ nitrogen content. From our experience of $In_xGa_{1-x}As/GaAs$ quantum wells we would expect a sensitivity equating to a few per cent In content. In the absence of 002DF contrast we would therefore place a limit for the variation in composition of $<1\%$ N and $\ll 5\%$ In. In contrast to the 002DF reflection, the large difference in atomic size of the GaInNAs alloy constituents ($r_N = 0.75$ Å, $r_{In} = 1.67$ Å, $r_{Ga} = 1.22$ Å, $r_{As} = 1.25$ Å), these composition fluctuations produce relatively high distortions in the lattice parameter of the alloy, a fact that is revealed with 220BF reflection.

Phase separation phenomena in thin epitaxial films are mostly due to surface reorganization of the adatoms into separate phases. The kinetics of this process are not well understood, but are believed to be strongly dependent on the surface diffusion of adatoms. The separate phases are then 'frozen' into the bulk film since the bulk diffusion rates are several orders of magnitude lower than those on the surface. Surface diffusion of adatoms is an activated process with an activation energy ∼0.2–0.3 eV, which equates to almost two orders of magnitude reduction over the temperature range 460–360 °C, sufficient to account for the decrease in both the period and magnitude of the composition modulation observed with decreasing growth temperature in GaInNAs quantum wells. As the GaInAs structures appear more homogeneous, the diffusion of adatoms must be enhanced in the presence of N atoms. Our PL results have shown that the changes in phase separation in the GaInNAs alloy observed when varying the growth temperature in the range considered do not affect considerably the intensity and wavelength of the emission peak. However, the peak is progressively broadened when the temperature is increased from 360 °C to 460 °C, associated with the increase in compositional fluctuations. Tournié *et al* [18] found that the low efficiency in photoluminescence of GaInNAs heterostructures is due to the low growth temperatures used and not to the N per se. We have found that the introduction of N in the alloy produces a progressive change in the microstructure when varying the growth temperature, which has the primary effect of broadening the PL peak. Phase separation seems to be an inherent characteristic of the epitaxial growth of GaInAsN quantum wells, at least at conventional epitaxial growth temperatures. Therefore, to optimize the optical properties of this alloy, a compromise should be reached between growth temperature and compositional fluctuations. A suitable growth temperature seems to be included in the range 400–460 °C for $Ga_{0.62}In_{0.38}N_{0.023}As$ multi-quantum wells obtained in our growth conditions.

4.2. Stranski–Krastanow growth mode

The 3D or Stranski–Krastanow (SK) growth mode observed in our study shows a similar tendency in both GaInAs and GaInNAs alloys. Whereas, growing at relatively low temperature the wells appear perfectly flat, on increasing the temperature the growth mode changes from 2D to 3D. However, the temperature at which the bi-dimensionality is lost is different in both systems. At 460 °C the GaInAs wells

remain flat, but in comparison the GaInNAs wells show well-defined islands. The Stranski–Krastanow growth mode [19] has been demonstrated to take place in highly mismatched systems [20, 21] as a mechanism to relax the strain in the epilayer [22]. Thermodynamic models have been widely used to predict its stability by considering the balance of strain and surface energies [23]. However, as the growth process per se is a non-equilibrium process, other factors such as deposition rate [24], temperature [24, 25] and diffusion [25] must also be considered. Our results have shown that, although in both $Ga_{0.7}In_{0.3}As$ and $Ga_{0.62}In_{0.38}N_{0.023}As$ alloys the Stranski–Krastanow growth process is thermodynamically favoured, it is kinetically limited by the growth temperature. In the GaInNAs quantum wells the critical temperature for it to take place is lower. Therefore, it should be a N-related phenomenon which promotes the 3D growth at lower temperatures and not the strain difference.

Classical theories of SK growth consider that an initially flat epilayer would evolve into 3D islands only when the first nuclei of material reach a particular critical size [23, 26], otherwise these nuclei dissolve back into the 2D layer. This implies that an energetic barrier is present which needs to be overcome for the stabilization of the first islands. As our results have shown, whilst the GaInAs structures are quite homogeneous, the GaInNAs quantum wells show phase separation. The presence of composition fluctuations is expected to produce non-uniformities in the surface strain of the structure. These variations in surface strain could locally reduce the energy barrier for the transformation into stable islands, favouring the 3D growth at lower temperature in the GaInNAs structures. This mechanism is analogous to that acting in stacked quantum dots, in which the stress from the underlying dots promote subsequent layers to stack above this position.

On the other hand, it has recently been proposed theoretically and demonstrated experimentally that the segregation of In from the flat wetting layer to the surface of the structure controls island formation [27, 28]. Taking into account this theory and according to our results, a possible mechanism would be that In segregation towards the surface is more favoured in the GaInNAs system than in GaInAs. Increased In segregation in the nitrogen-containing alloy would seem reasonable if we consider spontaneous formation of N-rich surface layers [29]. In the GaInNAs alloy, there is a large difference in atomic size between the constituent atoms (as mentioned previously). Placing the small N atoms in the atomic sites of the larger As atoms should produce local stresses in the structure. Diffusion towards the surface of the structure of an atom of large size such as In could be enhanced because of these stresses in the alloy, then favouring the formation of islands according to the model mentioned above [27, 28].

Both the two mechanisms considered could contribute to the Stranski–Krastanow growth in GaInNAs alloys. However, we believe that the main reason for the 2D–3D transition taking place at a lower temperature in GaInNAs than in GaInAs is the non-uniformities in the surface of the nitride structure due to phase separation. Lowering the energy barrier for the formation of the first nuclei would result in the appearance of islands at lower temperature, as our results have shown. In addition, we know of no data on increased In segregation in GaInNAs QWs and therefore favour the former model.

Finally, the anomalous behaviour observed in the first well of the samples grown at 400 °C and 440 °C is worth mentioning. They show a Stranski–Krastanow growth mode whilst the subsequent wells remain flat. Since the wells in each of these samples have the same composition and therefore the same lattice mismatch with the substrate, this difference is hard to explain by strain considerations. We think that the origin of this morphology should lie behind a change in the growth conditions of these wells with regard to the rest of the sample. We propose two possible causes. The first one is that the growth temperature was not stable at the low temperature when growing these wells, given that we have observed that slightly higher growth temperatures result in 3D growth. Recently, using emissivity corrected pyrometry, we have observed substrate temperature transients in MBE of several minutes after reducing the temperature before the growth of the quantum wells. The second possibility is that the initiation of the plasma source, which takes place a few nm before the first barrier, induces damage to the first well through nitridation of the underlying structure which is smoothed out in the subsequent growth. Initial experiments have suggested that both these factors may be responsible for this behaviour.

5. Conclusion

In this work, we have studied by TEM and PL the influence of growth temperature on GaInNAs and GaInAs quantum wells. Our results show experimental evidence for the existence of a phase separation in all the GaInNAs wells, enhanced when increasing the growth temperature. The behaviour is qualitatively similar to that seen in GaInAs of equivalent misfit, but with a lower growth temperature. We propose that the surface diffusion of adatoms is enhanced in the case of the nitrided sample. A broadening of the PL peak when raising the growth temperature in the GaInNAs structures has also been found, therefore the phase separation could be responsible for the degradation of the optical properties. Furthermore, it has been observed that although thermodynamically favoured, the Stranski–Krastanow growth mode in both materials is kinetically limited by temperature. The critical growth temperature for the 2D–3D transition is smaller in the GaInNAs material (440–460 °C) than in GaInAs (460–515 °C). Hence, the introduction of nitrogen favours a Stranski–Krastanow growth mode. Non-uniformities in the surface of the GaInNAs quantum wells as a result of the compositional modulations are proposed to locally lower the energy barrier for stable island nucleation.

Acknowledgments

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

References

[1] Temkin H, Coblentz D, Logan R A, van der Ziel J P, Tanbun-Ek T, Yadvish R D and Sergent A M 1993 *Appl. Phys. Lett.* **62** 2402

[2] Harris J S 2002 *Semicond. Sci. Technol.* **17** 880
[3] Kondow M and Kitatani T 2002 *Semicond. Sci. Technol.* **17** 746
[4] Wei S-H and Zunger A 1996 *Phys. Rev. Lett.* **76** 664
[5] Nakahara K, Kondow M, Kitatani T, Larson M and Uomi K 1998 *IEEE Photon. Technol. Lett.* **10** 487
[6] Reinhardt M, Fischer M, Kamp M, Hofmann J and Forchel A 2000 *IEEE Photon. Technol. Lett.* **12** 239
[7] Egorov A, Bernklau D, Livshits D, Ustinov V, Alferov Z and Riechert H 1999 *Electron. Lett.* **35** 1643
[8] Riechert H, Geelhaar L, Ebbinghaus G, Lima A, Ramakrishnan A and Steinle G 2003 *Conf. P. Indium Phosph.* p 3
[9] Geisz J F and Friedman D J 2002 *Semicond. Sci. Technol.* **17** 769
[10] Chang P C, Baca A G, Li N Y, Xie X M, Hou H Q and Armour E 2000 *Appl. Phys. Lett.* **76** 2262
[11] Spruytte S G, Coldren C W, Harris J S, Wamplet W, Krispin P, Ploog K and Larson M C 2001 *J. Appl. Phys.* **89** 4401
[12] Egorov A Y *et al* 2001 *J. Cryst. Growth* **227–228** 545
[13] Mars D E, Babic D I, Kaneko Y, Chang Y L, Subramanya S, Kruger J, Perlin P and Weber E R 1999 *J. Vac. Sci. Technol.* B **17** 1272
[14] Bi W G and Tu C W 1997 *Appl. Phys. Lett.* **70** 1608
[15] Xin H P and Tu C W 1998 *Appl. Phys. Lett.* **72** 2442
[16] Tournée E, Pinault M-A and Guzmán A 2002 *Appl. Phys. Lett.* **80** 4148
[17] Howie A and Whelan M 1961 *Proc. R. Soc. Lond.* A **263** 217
[18] Tournié E, Pinault M-A and Guzmán A 2002 *Appl. Phys. Lett.* **80** 4148
[19] Stranski I N and Krastanow L 1938 *Sitz.ber., Akad. Wiss. Wien, Math.-Nati.wiss. Kl., Abt.* 2B **146** 797
[20] Capellin G and De Seta M 2003 *J. Appl. Phys.* **93** 291
[21] Rosenauer A, Oberst W, Litvinov D and Gerthsen D 2000 *Phys. Rev.* B **61** 8276
[22] Tersoff J and LeGous F K 1994 *Phys. Rev. Lett.* **72** 3570
[23] Shchukin V A, Ledentsov N N, Kopèv P S and Bimberg D 1995 *Phys. Rev. Lett.* **75** 2968
[24] Johansson J and Seifert W 2002 *J. Cryst. Growth* **234** 139
[25] Osipov A V, Kukushkin S A, Schmitt F and Hess P 2001 *Phys. Rev.* B **64** 205421
[26] Tersoff J and LeGous F K 1994 *Phys. Rev. Lett.* **72** 3570
[27] Walther T, Cullis A G, Norris D J and Hopkinson M 2001 *Phys. Rev. Lett.* **86** 2381
[28] Cullis A G, Norris D J, Walther T, Migliorato M A and Hopkinson M 2002 *Phys. Rev.* B **66** 081305
[29] Zhang S B and Wei S-H 2001 *Phys. Rev. Lett.* **86** 1789