Composition fluctuations in GaInNAs multi-quantum wells

M. Herrera, D. González, R. García, M. Hopkinson, P. Navaretti, M. Gutiérrez and H.Y. Liu

Abstract: GaInNAs/GaAs(001) multi-quantum wells grown by MBE at temperatures in the range 360–460 °C have been studied by transmission electron microscopy and photoluminescence. The authors have observed the existence of periodic contrasts with 220BF reflection, which appear more pronounced when increasing the growth temperature. These strain contrasts have been associated to composition fluctuations in the wells and, therefore, it is suggested that an enhancement of the phase separation in the GaInNAs quantum wells occurs when varying the growth temperature from 360 °C to 460 °C. The photoluminescence results show a broadening of the emission peak over a similar growth temperature range. Thus, the degradation of the optical properties in the GaInNAs structures is suggested to be linked to the composition fluctuations.

1 Introduction

Much effort has been focused on the investigation of the GaInNAs system since Kondow *et al.* [1] proposed and created this revolutionary alloy in 1995 for application to long-wavelength (1.3–1.55 μm) laser diodes. The merit of this material is an unusually large negative bandgap bowing that allows the extension of the emission wavelength by adding small amounts of N to III–V alloys. The small size of N atoms provides also the possibility of reducing the lattice parameter of GaIn(N)As layers, reducing the lattice mismatch with GaAs substrates. It is thought that this alloy would substitute for the classical system GaInAsP/InP in laser diodes, which suffers from a high-temperature sensitivity of the threshold current and needs the use of thermoelectric cooling.

However, the challenge in the growth of this alloy GaInNAs is that the solubility of N into GaInAs is very low [2], and consequently there is a tendancy to phase separation. The degradation of the photoluminescence emission when adding N to GaInAs alloys has been widely reported [3]. To avoid the phase separation phenomena, the use of low growth temperatures has been suggested. Nevertheless, the relationship between composition fluctuations and growth temperature is not really clear. Our work is focused on the structural and optical properties of GaInNAs quantum wells grown at different temperatures in the range 360–460 °C.

2 Experimental

Four GaInNAs samples were grown in a VG V80H molecular beam epitaxy (MBE) system equipped with an Oxford Applied Research HD25 radiofrequency 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. The samples consist of five GaInNAs quantum wells (QWs) 8-nm-thick, with In and N contents of 0.38 and 0.023, respectively, sandwiched between $GaAsN_{0.007}$ barriers. The GaInNAs quantum wells were grown at different temperatures in each sample: 360 °C, 400 °C, 440 °C and 460 °C.

Samples were prepared for transmission electron microscopy (TEM) by mechanical thinning followed by ion milling for cross-section (XTEM) and planar view (PVTEM) observation. The TEM study was performed using a JEOL 1200EX transmission electron microscope operating at 120 kV. The samples were also studied by photoluminiscence (PL) using He–Ne excitation and a monochromator equipped with an GaInAs array detector.

3 Results

220BF transmission electron microscopy images of the sample grown at 360° have shown the absence of structural defects. Slight strain contrasts have been found in all the wells, and 002DF reflection exhibited that these QWs are perfectly flat. Similar structural features have been observed for the samples grown at 400 °C and 440 °C, but in these cases the strain contrasts revealed with 220BF reflection are progressively more intense, as can be observed in Fig. 1. The anomalous undulated behaviour of the first well in both samples should be noted. Moreover, in the structure grown at 440 °C, some dislocations coming just from this first well have been observed. Finally, increasing the growth temperature to 460 °C, the $Ga_{0.062}In_{0.038}N_{0.023}As$ quantum wells appear undulated, with a period of 20 nm, and also threading dislocations have been observed. The strain contrasts revealed with 220BF reflection for this sample are the most intense in our study.

Figure 2 shows the PL spectra of the samples investigated in this work. Narrow and intense peaks in the region near to 1.3 μm corresponding to the structures grown at 360 °C and 400 °C can be clearly seen. For the sample grown at 400 °C, a shoulder at higher wavelength is also observed, probably

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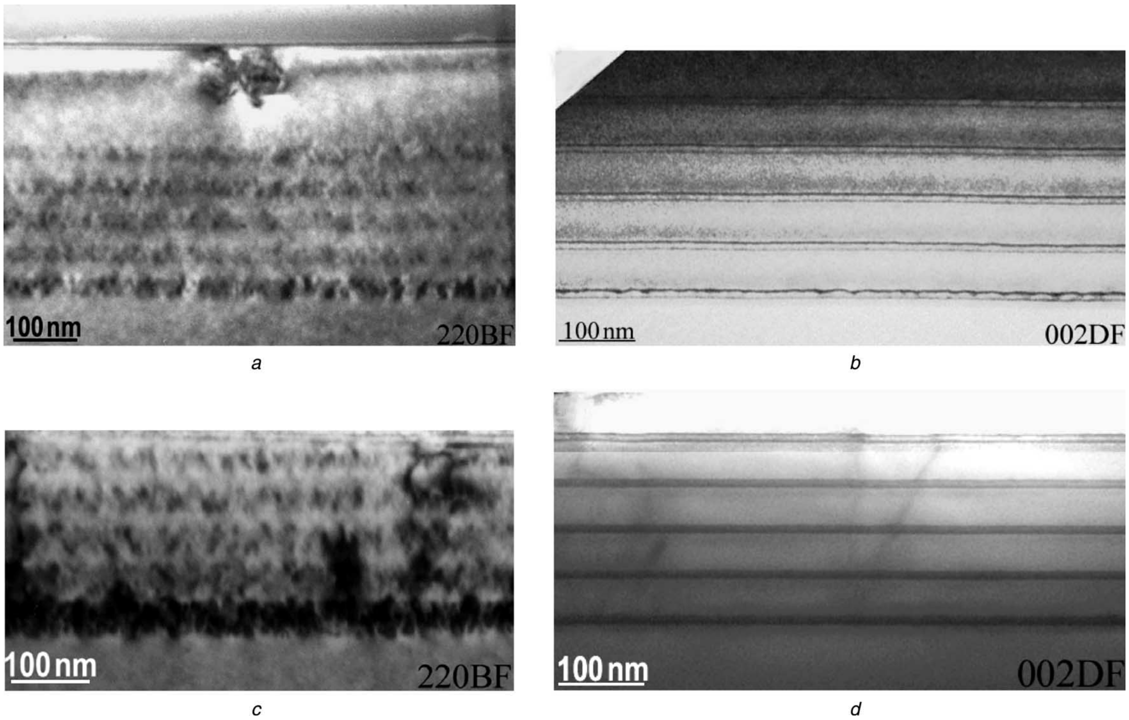

Fig. 1 *TEM micrographs of the samples grown at 400 and 440 °C obtained with 220BF and 002DF reflection*

a 220BF, $T_g = 400\,^\circ C$
b 002DF, $T_g = 400\,^\circ C$
c 220BF, $T_g = 440\,^\circ C$
d 002DF, $T_g = 440\,^\circ C$

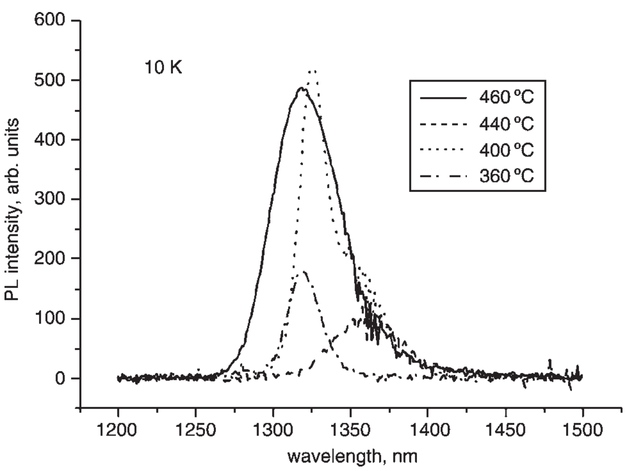

Fig. 2 *PL spectra of the studied samples*

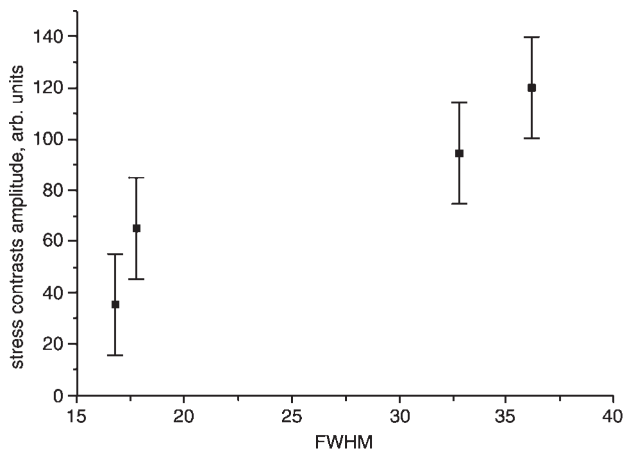

Fig. 3 *Plot of amplitude of strain contrasts taken from intensity profiles against FWHM in the PL spectra*

due to the irregular features in the first well. 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 the first well, as observed by TEM. Finally, the sample grown at 460 °C exhibits a high-intensity peak, broader than that of the previous structures.

In order to find a relationship between the structural and optical properties in these samples, diffraction contrast intensity profiles from the upper well in the 220BF TEM micrographs were collected. This showed an increase in the amplitude of the profile when raising the growth temperature from 360 °C to 460 °C, as observed qualitatively in the micrographs. The influence of the growth temperature on the structural properties of these samples could be related to the broadening of the photoluminescence peaks. Figure 3 exhibits a plot of the average height variation in the profile against the full width at half maximum (FWHM) of the PL peak for each sample. As can be observed, a correlation between both characteristics has been found, given that the emission peak is broadened when the strain contrasts are more prominent.

4 Discussion

We have found strain contrasts with 220BF reflection in all the studied GaInNAs quantum wells. To explain the origin of these contrasts, we need to consider electron scattering in a deformed crystal. The intensity of the incident and scattered waves in a non-perfect crystal can be related to the displacement field $R(r)$ of the constituent atoms [4], and changes in the intensity of these electron beams lead to the contrasts observed in the transmission electron microscope. Alterations in the lattice sites of the atoms produced by defects, such as dislocations, or by the distortion that usually suffer the atomic planes of an epitaxial coherent thin layer can give place to a displacement field $R(r)$ in the material. The GaInNAs quantum wells considered in our study have all the same composition and consequently the same lattice mismatch with the substrate. Hence, in the absence of lattice defects, the distortion of the atomic planes in the material, because of the local lattice mismatch, gives rise to strain contrasts. Our results have shown that the contrasts in the quantum wells are more pronounced on increasing the growth temperature. Moreover, although the structure obtained at 460°C shows 3-D growth, samples grown at 360°C, 400°C and 440°C do not exhibit any structural feature at our resolution level that could be responsible for such contrasts. Therefore, the origin of the contrasts revealed with 220BF reflection should lie behind the distortion of the atomic planes in the <110>directions.

Vegard's law establishs a relationship between the lattice parameter of a material system and its composition. This means that local variations of composition inside an alloy would bring about a modulation of its lattice parameter and, thus, the appearance of a displacement field in the atomic planes. We believe that the contrasts observed with 220BF reflection are due to composition fluctuations in the wells because of In/Ga interdiffusion at increasing growth temperature. There could be equivalent intermixing on the anion site, but the low N composition makes such effects difficult to resolve. Our results show an increase in the composition fluctuations of the alloy when increasing the growth temperature.

The analysis above about the existence of composition fluctuations in our GaInNAs quantum wells is based on the 220BF reflection. However, it is worth noting that the 002DF reflection offers higher compositional sensitivity, with an intensity dependent on the difference between the atomic structure factors of the constituent atoms. However, we have not found noticable contrasts with this 002DF reflection in our GaInNAs samples, which suggests that the magnitude of the phase separation should be very low. Owing to the large differences in atomic size of the GaInNAs alloy constituents, relatively small phase separations can produce relatively high distortions in the lattice parameter of the alloy, a fact that is revealed with 220BF reflection.

Generally, the appearance of composition fluctuations in thin epitaxial films has been attributed to surface reorganisation of the adatoms into separate phases by a surface diffusion process. 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. The activation energy of the surface diffusion of adatoms is approximately 0.2–0.3 eV, which equates to almost two orders of magnitude reduction over the temperature range 460–360°C. This could explain the decrease in the magnitude of the composition modulation observed with decreasing growth temperature in our GaInNAs quantum wells. However, we have found that the composition fluctuations could have an influence on the optical properties of this alloy. As shown in Fig. 3, the increase in the amplitude of the strain contrasts is accompanied by a broadening of the photoluminescence peak, whilst the intensity or peak wavelength is largely unaffected. However, in relation to this, it has been reported [5] that the low efficiency in PL of GaInNAs heterostructures can, in part, be due to the low temperatures used in the growth and may not be directly linked to the incorporation of N. Our results have shown that besides the growth temperature, composition fluctuations due to N or In diffusion can degrade the emission properties of this alloy. Composition fluctuations seem to be an inherent feature of GaInAsN quantum wells, at least at the classical epitaxial growth temperatures. Therefore, to optimise the optical properties of this alloy, a compromise should be reached between growth temperature and compositional fluctuations.

It is worth mentioning the anomalous behaviour observed in the first well of the structures grown at 400°C and 440°C, which show some undulations, while the subsequent wells remain flat. The first well in each of these structures has the same lattice mismatch with the substrate as the others and, therefore, this different behaviour could not be explained by a difference in strain. We think that the cause of the change in morphology may be a variation in the growth conditions of this first well with regard to the other four wells in the sample. Two possible causes are considered. The first one is that the growth temperature was not stable at the low temperature when growing these wells, given that we have observed in our sample grown at 460°C that an increase in the growth temperature results in 3-D growth. Recently, using emissivity corrected pyrometry, we have observed substrate temperature transients in MBE of several minutes duration 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 in part responsible for this behaviour.

5 Conclusions

The structural and optical properties of GaInNAs quantum wells when varying the growth temperature in the range 360–460°C have been investigated. We have observed periodic strain contrasts in all the wells with 220BF reflection. The magnitude of these contrasts is higher when increasing the growth temperature, as exposed by the intensity profiles. Although the sample grown at 460°C has shown some undulation of the wells, the other samples have not exhibited any structural changes that could account for these contrasts. We have concluded that they are due to composition fluctuations in the wells, enhanced when increasing the growth temperature. With regard to the photoluminescence results, the emission peak is progressively broadened when increasing the growth temperature. This broadening has been correlated to the composition fluctuations. Therefore it is suggested that this change in the microstructure of the system could degrade its optical properties.

6 Acknowledgments

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