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Thin Solid Films 483 (2005) 185–190

thin solid films

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Structural and optical properties of high In and N content GaInNAs quantum wells

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Received 15 April 2004; accepted in revised form 16 January 2005
Available online 23 February 2005

Abstract

We have analysed by Transmission Electron Microscopy and Photoluminescence (PL) the structural and optical properties of $Ga_{1-x}In_xN_yAs_{1-y}$ quantum wells with Indium and Nitrogen contents in the range $0.20<x<0.35$ and $0.013<y<0.023$, respectively. Our results have shown that a degradation of the structural quality of the wells when increasing the In content takes part in two distinct steps. In the first one, an undulation of the surface of the wells on raising the In content from 20% to 25% has been observed. This is accompanied by the appearance of a high density of extrinsic dislocation loops, probably due to a high local stress concentration in the material. For these samples the PL spectra show intense and narrow emission peaks at 1.1–1.2 μm, therefore the existence of dislocation loops seems not to affect considerably the optical efficiency of the material at this stage. In a second step, on increasing the In composition to 35%, the PL emission efficiency of the wells is severely degraded and the samples show the appearance of threading dislocations. An unfaulting of the dislocation loops as a consequence of a coalesce reaction with two Shockley partials is proposed as the mechanism for the formation of the observed threading dislocations.

PACS: 61.16.Bg; 61.72Dd; 61.72Ff; 61.72Lk; 61.82Fk; 68.65.+g; 78.20.-e; 78.55.-m; 78.55Cr
Keywords: Photoluminescence; Transmission electron microscopy; GaInNAs; Molecular beam epitaxy

1. Introduction

Semiconductor lasers at 1.3 and 1.55 μm wavelength are very important light sources for optical fibre communications. In 1995, Kondow et al. [1] proposed and created a novel material, dilute nitride GaInAs, for potential application within optoelectronic devices for this wavelength range. GaInNAs is a solid solution with a large band-gap bowing which offers the possibility of reducing drastically the GaInAs bandgap by the addition of relatively small N contents (<5%). Therefore, laser emission at 1.3 μm can be produced from quantum wells of GaInNAs with an In content of ~30% and a N composition of ~2%. This material system offers the advantages of GaAs based substrate technology and is very promising to overcome the poor temperature characteristics of conventional InP long wavelength laser diodes [2]. The GaInAsN material system has also been successfully used for vertical cavity surface emitting lasers [3] as well as solar cells [4] and heterobipolar transistors [5]. An additional advantage of the GaInNAs alloy is that the small size of the N atoms reduces the lattice mismatch of GaInAs with respect to the GaAs substrate and therefore fewer structural defects are expected for a fixed N concentration. However, the large differences between the bond energy and the electronegativity arising from the substitution of N on the group V site may be expected to give rise to additional localised defect formation or to phase separation. These effects may be even stronger if nitrogen has a preferred local bonding arrangement with In or Ga, or if N clusters with itself [6].

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doi:10.1016/j.tsf.2005.01.016

Table 1
In and N contents of the GaInNAs structures studied in the present work. The lattice mismatch with the substrate (f) is also included

Sample	% In	% N	f (%)
A20	20	1.3	1.17
B20	20	1.9	1.06
A25	25	1.6	1.47
A35	35	1.4	2.23
B35	35	2.3	2.05

There have been relatively few studies on the structural defects that appear when increasing the In or N content of GaInNAs alloys. Our work is focused on the structural and optical properties of GaInNAs quantum wells with increasing In content, studied by Transmission Electron Microscopy (TEM) and Photoluminescence (PL). The characterization of the crystalline defects allows us to propose the sequence of defect generation and its relationship with the optical degradation of the structures.

2. Experimental details

Five GaInNAs samples were grown on (001) GaAs substrates in a VG V80H Molecular Beam Epitaxy 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 (XRD) analysis of bulk samples and GaNAs quantum wells grown using similar plasma emission intensities. The nitrogen contents determined by XRD were checked in a number of cases by Secondary Ion Mass Spectrometry and found to be consistent within experimental error. The samples studied consisted of five GaInNAs quantum wells (QWs) grown at 460 °C with varying In and N compositions as shown in Table 1, embedded between $GaAsN_{0.007}$ barriers. The lattice mismatch of the quantum wells with the GaAs substrate in each sample is also shown in Table 1. The thickness of the QWs was 8 nm, and that of the barriers was 52 nm.

Samples were thinned to electron transparency for Transmission Electron Microscopy (TEM) by mechanical polishing followed by low voltage Ar^+ milling at a liquid nitrogen cooled stage for cross section and planar view observation. The TEM study was performed using a JEOL 1200EX transmission electron microscope operating at 120 kV. The samples were studied by Photoluminescence at room temperature using a wavelength dispersive system, 633 nm He-Ne laser excitation and an InGaAs detector.

3. Results

Both samples with an In content of 20% (A20 and B20) have shown by Transmission Electron Microscopy a good quality microstructure, with no structural defects and flat wells despite the differences in nitrogen content (1.3 and 1.9%). However, on increasing the In content to 25%, with the lattice mismatch, f, increasing from 1.1 to 1.4 (sample A25), we have observed a change in the surface morphology of the wells, which becomes undulated (Fig. 1a). The period of the undulations is approximately 20 nm. In structure A25, small dislocation loops have been found in all the wells, with size of 20–30 nm. The characterization of these loops by means of the inside-outside contrast criterion has given as a result that they are extrinsic, i.e., they contain an extra layer with regard to the perfect arrangement of the crystal.

TEM micrographs of samples A35 and B35, which contain the highest In content in our study (35%) and therefore have the highest lattice mismatch (2.23 and 2.05, respectively), show that the surface of the wells are also undulated. The period of the undulations is similar to that of the previous structure. Dislocation loops have also been observed (Fig. 1b), but in this case they are accompanied by threading dislocations (TDs) and even some stacking faults have been found. It should be noted that misfit dislocations have not been observed in these samples. The TDs originate from the upper QWs and, in general, they appear to be grouped into two or three lines that originate from the same region (see Fig. 2). The density of TDs is non-uniform in

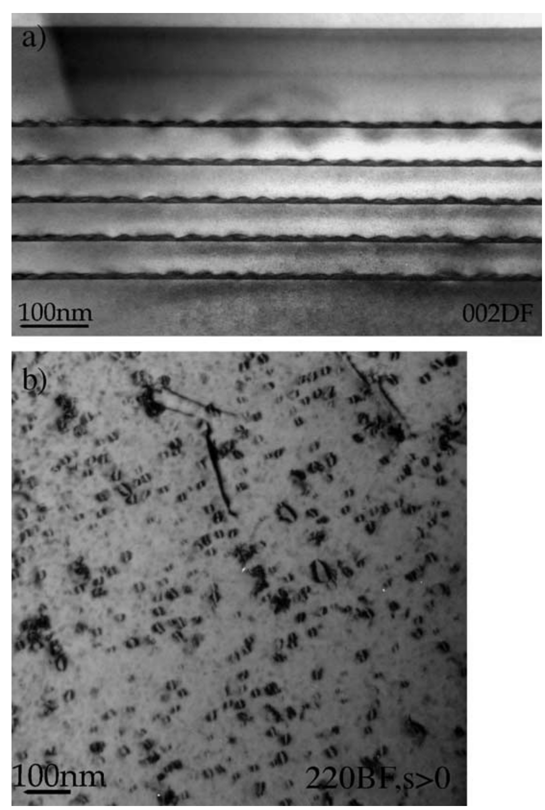
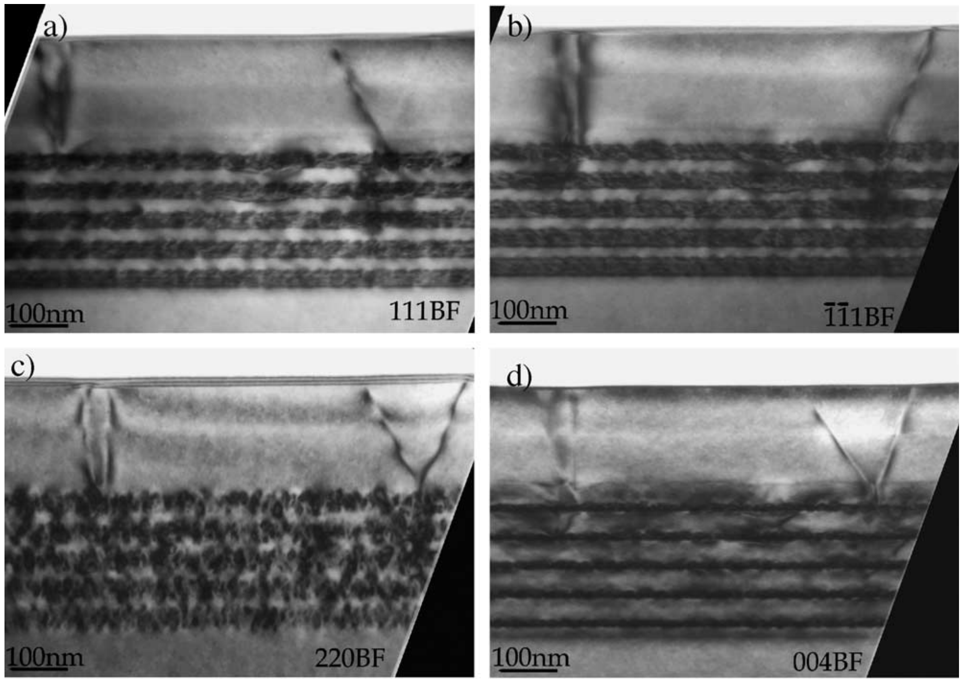


Fig. 1. a) 002DF cross section micrograph of sample A25, showing undulations of the GaInNAs QWs with period 20nm. b) 220BF planar view micrograph with $s>0$ of the structure A35, where Frank dislocation loops are observed.



e)

	g*b for the following g			
b	[220]	[004]	[111]	[$\bar{1}\,\bar{1}\,1$]
$\frac{1}{2}[110]$	2	0	1	-1
$\frac{1}{2}[101]$	1	2	1	0
$\frac{1}{2}[01\bar{1}]$	1	2	0	-1

Fig. 2. Cross section micrographs of sample B35 with a) [111], b) [$\bar{1}\bar{1}$1], c) [220] and d) [004] reflections, e) Invisibility criterion for the study in [$\bar{1}$10] direction of our GaInNAs/GaAs(001) samples.

both structures. For sample A35, the measured density of TDs is 3–4$\times10^9$ cm^{-2}, whereas in B35, with a smaller lattice mismatch due to the higher N content, the dislocation density is a somewhat lower, being 1–2$\times10^9$ cm^{-2}, approximately. The Burgers vector of the threading dislocations have been characterized by means of the invisibility criterion as shown in Fig. 2 as $(1/2)a\langle110\rangle$. Surprisingly, although around two thirds of the observed TDs show the classical 60°-out Burgers vector (out of the growth plane, and in our case 27% are $(1/2)a\langle101]$ whilst 38% are $(1/2)a\langle011]$), the remaining 35% of these dislocations exhibit the 60°-in Burgers vector configuration, $((1/2)a)\langle110]$), which is parallel to the growth plane. The unusual results of our Burgers vector analysis mean that the formation of these TDs may not follow the traditional Mathews and Blakeslee mechanism [7], as will be discussed later.

Fig. 3 shows the photoluminescence data at room temperature of the studied samples. As it is clearly seen, samples A20, B20 and B25 shows PL peaks at wavelengths in the range 1.1–1.2 μm. On increasing the In content to 35%, the emission wavelength is extended to 1.3 μm for A35 and to 1.4 approx. for B35. However, the emission efficiency is very much degraded at these high In compositions, diminishing the intensity down to a few percent of the low In samples. We suggest that this strong

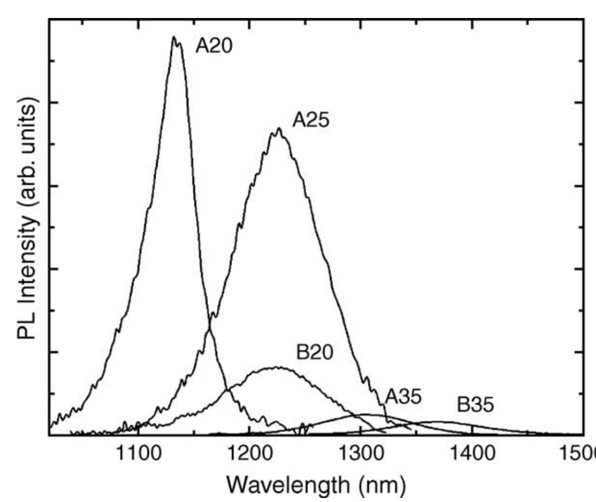


Fig. 3. PL data from the studied samples.

quenching is related to the observation of the structural defects in the TEM.

4. Discussion

Our TEM study of the effect of the In content in GaInNAs QWs has shown, in the first instance, a change in the morphology of the wells from flat to undulated when raising the In composition from 20% to 25%. This is the classical behaviour of high In content GaInAs structures [8]. However, this change in surface morphology has been reported to take place at a lower In compositions in the dilute nitrides than in GaInAs, despite the reduced strain, due to phase separation into In-rich and In-deficient regions [9]. Our results have revealed that, in the case of GaInNAs structures, the undulation of the QWs is accompanied by the formation of small Frank dislocation loops. We believe that the appearance of these loops is directly linked to the 3D morphology. Dislocation loops are usually formed when high levels of stress are concentrated in local areas of the material. This explains its formation for undulated GaInNAs QWs (25% and 35% In structures) and not for the flat wells (20% In samples). However, although dislocation loops have been widely observed in quantum dot structures, they have not been commonly reported for undulated GaInAs QWs of similar compositions. Thus, their appearance in GaInNAs should be related to the introduction of N. Extrinsic Frank dislocation loops consist of a double stacking fault sequence. It could be that the addition of small amounts of nitrogen in the GaInAs alloy changes the stacking fault energy (SFE) of the material. The influence of N in the stacking fault energy has been calculated for metals such as fcc iron-based alloys (with Nitrogen content lower that 0.5%) [10], where it is predicted firstly an increase of SFE for low N content and then a rapid decrease of the SFE. We have not found theoretical or experimental predictions of the influence of N in the SFE for the GaInNAs alloy, but our results suggest a decrease of this stacking fault energy by the addition of 2% N in GaInAs structures. This fact, coupled with the high level of local stresses in the undulated GaInNAs QWs could favour the appearance of the Frank loops in our structures.

The second step in the degradation of the structural quality of these GaInNAs quantum wells have been found on raising the In content from 25% to 35%, when threading dislocations appear. The Burgers vectors of these TDs have been characterized by means of the invisibility criterion as $(1/2)a\langle 110\rangle$ as it is shown in Fig. 2. Although two thirds of these dislocations have the classical 60°-out configuration (with the Burgers vector out of the growth plane), unusually we have observed that 35% of these have the Burgers vectors parallel to the growth plane (60°-in). Typically, only 60°-out threading dislocations in epitaxial layers are considered in the Mathews–Blakeslee mechanism for the plastic relaxation of thin films, since they can glide forming new segments of misfit dislocations [7]. However, the critical thickness for dislocation formation predicted by this model is somewhat higher than the thickness of our GaInNAs quantum wells. Moreover, no misfit dislocations have been observed in these samples. On the other hand, in non-planar surfaces such as quantum dots or undulated quantum wells, it has been reported that the concentration of stress in the compression areas between the dots can cause the formation of small fragments of misfit dislocations that can later glide towards the surface forming a misfit segment [11]. Again, this mechanism cannot be taken into account because misfit dislocations have not been found in our GaInNAs structures. Furthermore, threading dislocations with the 60°-in Burgers vector could in no way be produced through the mechanisms described above. The reason for this is that misfit dislocations with Burgers vectors parallel to the growth plane are sessile to glide for misfit relief and therefore a different mechanism needs to act to explain our results. We propose that the threading dislocations observed in our high In content samples are formed from the dislocation loops observed in the low In samples through a mechanism of unfaulting. It has been widely reported that an extrinsic Frank loop can be unfaulted into a perfect loop by the coalescence reaction between two Shockley partials [12,13]. In our GaInNAs/GaAs(001) material, there are three different Shockley partials parallel to each {111} habit plane of a Frank loop, which is the requisite criterion to become involved in the unfaulting process. After the reaction, each pair of partial dislocations would then give rise to a perfect dislocation with different Burgers vectors:

$$\frac{a}{6}[\bar{1}2\bar{1}]+\frac{a}{6}[\bar{1}\bar{1}2]+\frac{a}{3}[111]\rightarrow\frac{a}{2}[011]$$

$$\frac{a}{6}[\bar{1}\bar{1}2]+\frac{a}{6}[2\bar{1}\bar{1}]+\frac{a}{3}[111]\rightarrow\frac{a}{2}[101]$$

$$\frac{a}{6}[2\bar{1}\bar{1}]+\frac{a}{6}[\bar{1}2\bar{1}]+\frac{a}{3}[111]\rightarrow\frac{a}{2}[110]$$

In principle, the probability of occurrence of these three reactions in the material is the same; consequently, the resulting experimental distribution would be composed of perfect dislocations with each of the Burgers vectors from those given above, each with a probability of one-third. This agrees with the experimental results obtained in the present study, therefore we conclude that the threading dislocations observed in the 35% In GaInNAs are the result of the unfaulting of the existing extrinsic loops into perfect loops and their subsequent glide towards the surface of the structure. The magnitude of the stacking fault energy corresponding to extrinsic loops is similar to that of intrinsic loops [14], therefore despite the fact that this is a double faulting process, we would not expect a relative thermodynamic dependence. According to our observations, the unfaulting of these loops should be related to the lattice mismatch of the structures. In the series of samples, TDs are absent in sample A25 (f=1.47) but present in A35 and B35 (f=2.23 and 2.05, respectively), with a higher density in the higher lattice mismatch sample A35. The differences in the lattice mismatch could influence the unfaulting process in its earliest stages.

In the literature there is no agreement on the process of formation of the two Shockley partials which participate in the reaction. Several mechanisms of intersection or coalescence with pre-existing perfect dislocations have been proposed [15,16]. For example, Song et al. [16] proposed the unfaulting of Frank loops by their intersection with a perfect dislocation, through the formation of a partial dislocation dipole separated by one atomic plane. In this way, the observed relation of f to the unfaulting process could lie behind the mechanism of the formation of Shockley partials. Further studies will be needed to understand this point.

We now turn to the photoluminescence results. The PL spectrum for the lowest In and N sample (A20), which shows the best microstructure, shows an intense PL and narrow peak at 1130 nm. Increasing the N content for the same In content (20%) increases the wavelength to beyond 1.2 μm and degrades the intensity and linewidth (sample B20). However, raising only the In content to 25% (sample A25) retains a high intensity. For In compositions of 35%, the PL peak exceeds 1.3 μm, but the intensity of the samples is degraded significantly compared to A20 and A25. The major structural difference between these samples is the presence of threading dislocations in the 35% In samples. For the sample with 25% In, undulations of the well as well as dislocation loops, were observed. However, the emission efficiency from this structure is high, despite the structural defects present in this sample. In this way, it seems that the influence of dislocation loops in the optoelectronic behaviour of this material is qualitatively different from that of threading dislocations, in that the dislocation loops appear not seriously degrading the properties of the GaInNAs wells. This is in contrast to the results obtained by Volovik et al. [17], who attribute the degradation of the luminescence intensity in GaInNAs samples to the appearance of dislocation loops. The influence of dislocation loops in the PL emission has been investigated for silicon structures [18] where paradoxly, the formation of these loops has been used as a tool to enhance the radiative emission in this material by encouraging localisation. It is reported that dislocation loops introduce a tridimensional strain field that modifies the bandgap of the structure, providing spatial confinement in three dimensions. If capture is encouraged at these sites, we must conclude that the dislocation loops do not act as significant non-radiative routes in these materials. However we must be careful to relate macroscopic PL measurements (spot size ~100 μm) to microstructure and microscopic PL measurements will be required to fully clarify this matter.

5. Conclusions

In this work, we have studied the influence of the In content on the structural and optical properties of GaInNAs QWs. The structural characterisation of these samples has shown that on increasing the In content from 20% to 25%, the quantum well structure becomes undulated. This change in morphology is accompanied by the appearance of extrinsic dislocation loops. The mechanism which enhances these loops may be related to a decrease in the stacking fault energy of the material when adding small amounts of N to GaInAs or to the localised high stresses in the structure because of the 3D morphology. On raising the In composition to 35% with the lattice mismatch, f, increasing to more than 2%, threading dislocations gliding to the structure surface are observed. The unfaulting of Frank loops by means of the reaction between two Shockley partials is considered as the mechanism of formation of these threading dislocations. The characterization by PL has shown intense peaks near to 1.2 μm for the structures with 20% and 25% In. The presence of dislocation loops seems not to affect considerably the emission efficiency of the structure. However, a strong degradation of the PL intensity peak has been observed in the higher lattice mismatch structures (f>2%). We believe this degradation is due to the presence of TDs formed from the unfaulting of the loops.

Acknowledgments

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

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