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# The growth and properties of GaN:As layers prepared by plasma-assisted molecular beam epitaxy

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## Abstract

We have studied the growth and properties of GaN:As layers prepared by molecular beam epitaxy, using a plasma source for active nitrogen. We have demonstrated that arsenic doping during growth produces films showing blue emission at room temperature. The blue emission is centred at 2.6 eV and is more than a decade stronger than the band edge emission. The films are predominantly wurtzite, but with a small cubic content which exists mainly close to the substrate–epilayer interface. We have investigated the influence of growth conditions on the intensity of this blue emission. In films grown under optimum conditions, the blue emission is strong enough to be clearly visible under normal room lighting. We have also discussed the transition from As-doped GaN showing blue emission to the formation of GaN<sub>1-x</sub>As<sub>x</sub> alloys. We have determined that for a fixed arsenic flux, increasing the N/Ga ratio leads to the formation of alloy films. Our results suggest that this materials system may have potential applications in electronic and opto-electronic devices.

## 1. Introduction

During the last few years there has been considerable theoretical interest in As-doped GaN [1–7] and experimental studies of the same system have emerged [8–31]. Three main reasons motivate such investigations—the abrupt decrease in the band gap for GaNAs solid solutions, the observation of blue emission at room temperature from arsenic-doped GaN and arsenic-stimulated growth of the cubic phase of GaN.

The large difference in lattice parameters for GaAs and GaN and in crystal structure leads to a very non-linear negative bowing of the GaNAs band gap versus composition, with a much

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larger bowing parameter than for more conventional III–V semiconductors alloys [1–4]. A large miscibility gap as a result of the large difference in lattice structure was theoretically predicted and experimentally confirmed for this Ga–N–As system. If one could produce GaNAs alloys over the whole composition range, they could be used for optical devices operating from the ultraviolet ( $\sim 0.4 \mu\text{m}$ ) to the infra-red ( $\sim 2 \mu\text{m}$ ).

A second reason for the recent interest in this alloy system is the existence of blue emission at room temperature from As-doped GaN. The first experimental evidence for the existence of such emission came in photoluminescence (PL) studies of GaN implanted with As, where a peak at 2.58 eV was observed [8]. More recently, such blue/green PL has been observed in samples of GaAs nitrided in  $\text{NH}_3$  [9] and in As-doped GaN grown by metal–organic vapour-phase epitaxy (MOVPE) [10–12].

The third reason for interest in this GaNAs system relates to the possibility of growing in a controlled manner cubic (zinc-blende) GaN. We have previously shown [18], and this has subsequently been confirmed for both molecular beam epitaxy (MBE) [19] and MOVPE [20], that under appropriate conditions, arsenic increases the amount of zinc-blende GaN and decreases the fraction of wurtzite material.

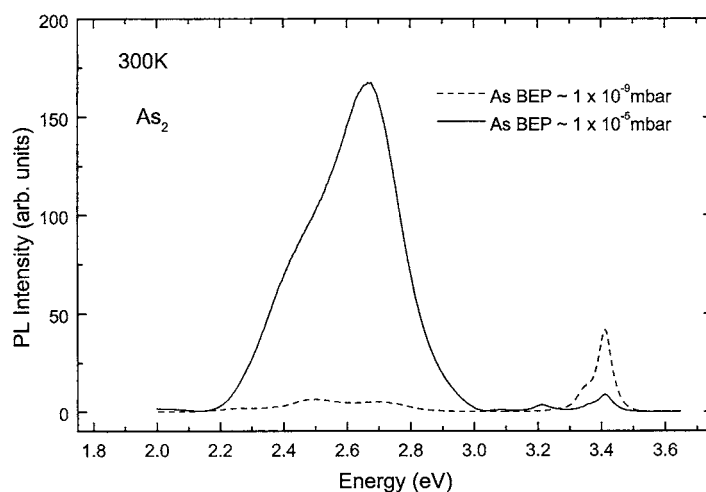
It has been shown that doping with As has a number of beneficial effects for both MOVPE [13–15] and MBE [16] of group III nitrides. Arsenic can both influence the surface reconstruction during growth [21, 22] and improve the surface morphology of the layers [23, 24]. Arsenic doping has also been reported to improve the PL of GaN grown by MOVPE, suppressing the yellow emission whilst at the same time increasing the intensity of the donor–acceptor pair emission at 3.28 eV [13] and improving additionally the electrical properties of GaN [14].

In this paper we report in detail the influence of arsenic on the optical and structural properties of GaN films grown by MBE.

## 2. Experimental details

The As-doped GaN layers used in this study were grown on sapphire substrates by MBE at a temperatures from 500 to 800 °C in a reactor, which has been described in detail elsewhere [26, 27]. The sample temperature was measured using an optical pyrometer. The sapphire samples were coated on the back with Mo. Active nitrogen for the growth of the group III nitrides was provided by an Oxford Applied Research (OAR) CARS25 RF activated plasma source, which is equipped with a silicon diode optical emission detector (OED). The signal from this OED is proportional to the amount of active nitrogen species coming from the source. The nitrogen flux was changed from  $1 \times 10^{-5}$  to  $5 \times 10^{-5}$  mbar beam equivalent pressure (BEP). Arsenic in the form of dimers ( $\text{As}_2$ ) or tetramers ( $\text{As}_4$ ) was produced using a two-zone purpose-built cell, and the arsenic fluxes were in the range from  $1 \times 10^{-9}$  to  $2 \times 10^{-5}$  mbar (BEP). Prior to the growth of the GaN layers, the sapphire substrates were nitrided at a temperature of about 800 °C for 30 min in the same MBE reactor. During this nitridation process and during the subsequent layer growth, the nitrogen plasma source was operated at 450 W.

All the samples were investigated using room temperature PL. The excitation source was a Kimmon HeCd laser operating at 325 nm. The maximum power of the laser at the sample surface was 9.4 mW. The surface morphology of the films was determined using atomic force microscopy (AFM). Film thickness was measured using optical reflectivity measurements. We have used a range of x-ray diffraction techniques to study the structural properties of the samples including simple  $\omega$ – $2\theta$  scans, 2D reciprocal-space maps and pole figures using a Philips X'Pert system. Secondary-ion mass spectroscopy (SIMS) studies were performed to



**Figure 1.** PL spectra from an undoped and an arsenic-doped film of GaN grown by MBE at about 800 °C.

determine the As concentration in the samples; implantation standards were used to calibrate the SIMS system for GaN.

### 3. Experimental results

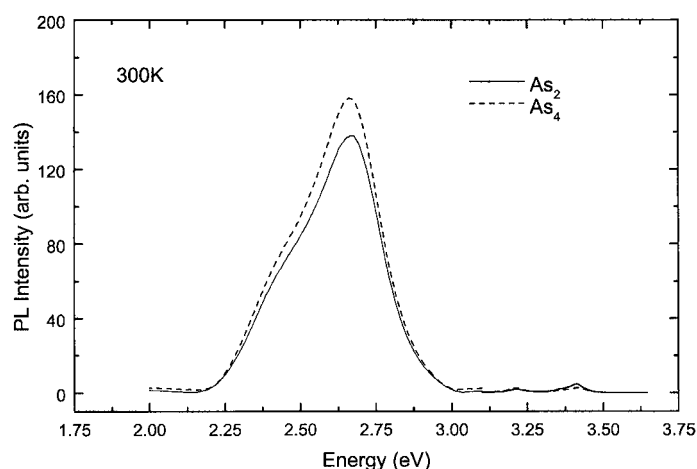
#### 3.1. Blue emission from As-doped GaN

The introduction of an arsenic flux during the growth of GaN films by MBE has a dramatic influence on the optical properties of layers. The low-temperature PL spectra from samples grown without arsenic show the usual donor bound exciton peak and at room temperature free exciton emission is observed as shown in figure 1. However, with an arsenic flux present, the PL spectrum is changed considerably, as shown in figure 1. Very strong blue emission at about 2.6 eV is observed at room temperature from As-doped GaN layers grown by MBE. The intensity of the blue emission from the As-doped samples is more than an order of magnitude stronger than the band edge emission in undoped GaN samples and can be seen in normal lighting. We also observe an additional peak close to the band edge of GaN at about 3.2 eV. The intensity depends strongly on the arsenic flux for both peaks [25, 26]. Very similar PL spectra are observed for GaN samples grown with either As<sub>2</sub> or As<sub>4</sub> fluxes of the same magnitude, as shown in figure 2; however, the dependences of the blue emission intensity on the dimer and tetramer pressure are not absolutely identical [25].

We observe strong blue emission at room temperature from As-doped GaN films grown at high temperatures (about 800 °C). However, we observe that as the substrate temperature is reduced, the intensity of this blue emission decreases and cannot be observed for samples grown at 500 °C, for the range of arsenic fluxes studied.

#### 3.2. The relation between arsenic incorporation into GaN layers and blue emission

Auger electron spectroscopy (AES) studies of the As-doped GaN films after growth at 800 °C show the presence of a small amount of As on the surface of the layers. The concentration of As measured by AES is almost independent of the As flux for a wide range of As BEPs from the background arsenic pressure of 10<sup>-9</sup> mbar to an arsenic flux of 10<sup>-5</sup> mbar and is practically the



**Figure 2.** Comparison of PL spectra from films grown at about 800 °C with  $\text{As}_2$  and  $\text{As}_4$  fluxes of approximately  $10^{-5}$  mbar.

same for  $\text{As}_2$  and  $\text{As}_4$ . This probably indicates that there is an equilibrium surface concentration of arsenic, which is formed by either adsorption during cooling or segregation to the surface during growth.

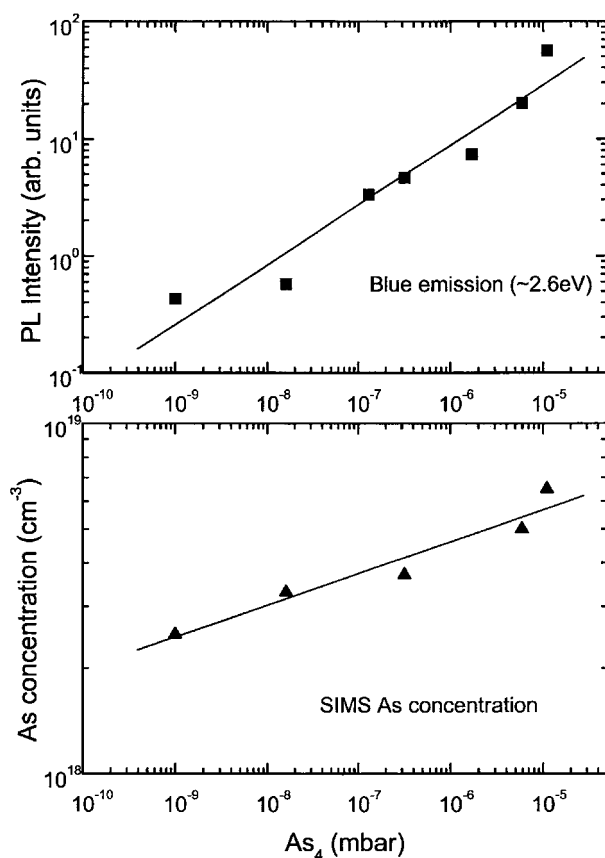
We have also studied the incorporation of arsenic into the bulk of the As-doped GaN films using SIMS. SIMS spectra from the As-doped GaN samples show that the As concentration is approximately constant with depth. The concentration of arsenic increases monotonically with increasing  $\text{As}_4$  flux during growth, as shown in figure 3. Surprisingly, we observe only about a factor 3 change in the arsenic concentration for a four decades change in the arsenic flux. The rate of increase of concentration with flux has a slope on a log–log plot of approximately 0.1.

Figure 3 also shows the dependence of the intensity of the blue PL peak at 2.6 eV on the arsenic flux. The slope of the line for the blue intensity versus arsenic flux (0.49) is significantly greater than the slope of the As concentration versus arsenic flux (0.1). This implies that the blue PL intensity depends very strongly on the As concentration in the GaN lattice, having an approximately fourth-power dependence.

The SIMS concentration shown in figure 3 corresponds to the total amount of arsenic in the GaN films. From SIMS data alone, we cannot easily determine the location of the As, which may exist on the Ga or N sublattices of GaN or as an interstitial. Our x-ray studies demonstrate that a small amount of GaAs is observed for the two highest arsenic fluxes, but for all the other samples, no GaAs is detected. From x-ray linewidths, we can estimate from Scherrer's formula that the size of the GaAs inclusions is about 50 nm [32]. Therefore, we may tentatively suggest that the dependence on arsenic flux of the arsenic incorporation into the GaN lattice is even lower than 0.1, because some of the arsenic measured by SIMS is present in the form of GaAs crystallites.

The weak dependence of the As incorporation into GaN as a function of the arsenic flux suggests that there is an unusual growth mechanism. A possible model which may explain this dependence is that arsenic is incorporated from a limited number of surface sites, whose density varies only very weakly on the arsenic flux. This model is consistent with our observations by AES, which also suggests that the surface concentration of arsenic does not depend on the arsenic flux.

The blue emission intensity at 2.6 eV depends more strongly on the arsenic flux than the concentration of As incorporated into the GaN. This in turn means that the PL intensity varies



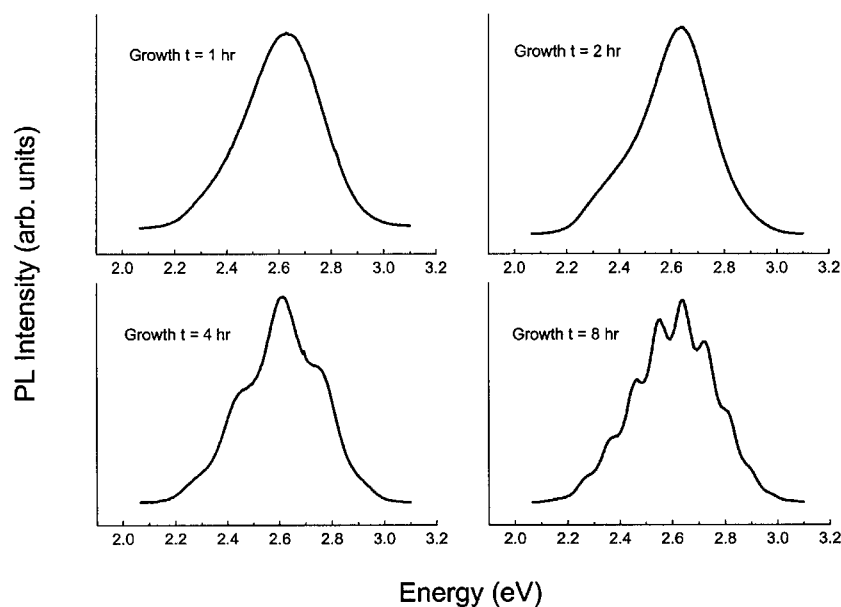
**Figure 3.** The PL intensity of the blue emission and the arsenic concentration measured by SIMS as a function of the arsenic flux used during MBE growth at about 800 °C.

very strongly with the concentration of As in the GaN lattice. If As is simply incorporated as a substitutional element, we would not expect such a strong dependence on the amount of As in the GaN. It is possible, therefore, that in addition to the direct influence of the arsenic incorporated into the lattice on the PL, the existence of the arsenic flux may change the stoichiometry of the GaN films grown using MBE. Thus the reason for the strong dependence of the blue emission intensity on the arsenic incorporation is still an open question.

### 3.3. The influence of sample thickness on the blue emission from As-doped GaN

We investigated the dependence of the optical properties of GaN films on sample thickness for both undoped and arsenic-doped layers. As expected, in both cases, there is a linear relation between the sample thickness and growth time, indicating that the growth rate remained constant for both sets of samples.

The structural properties of the samples were investigated by means of x-ray diffraction. The structural quality for both the undoped and the As-doped GaN improves with sample thickness. Using Scherrer's relation [32], from the x-ray data we see that for both sets of samples the size of the subgrains of our columnar material increases with increasing sample thickness, in good quantitative agreement with our AFM data. X-ray studies also show that the proportion of cubic GaN decreases rapidly with film thickness for both sets of samples. For



**Figure 4.** Blue emission from arsenic-doped GaN layers of different thicknesses grown at 800 °C at a growth rate of  $0.3 \mu\text{m h}^{-1}$ .

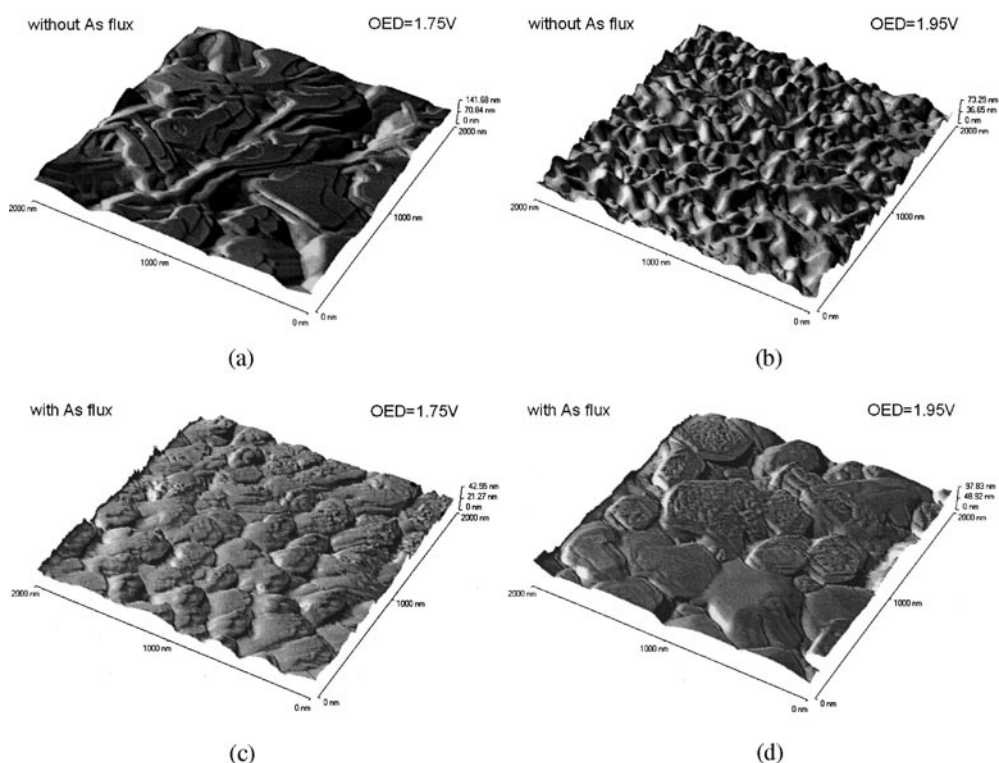
the undoped films the cubic fraction is almost entirely located close to the substrate–epilayer interface, but in the As-doped films the cubic content is initially higher at the substrate–epilayer interface and decreases more slowly with sample thickness.

Figure 4 shows the structure of the blue band region of the PL spectra as a function of film thickness. The intensity of blue emission varies with sample thickness, but for convenience the curves have been normalized. Independently of the film thickness, the blue emission is centred at about 2.6 eV. For the thinnest sample, only one peak is observed, but for thicker samples multiple peaks can be resolved. The number of peaks observed increases monotonically with sample thickness, indicating that the main factor involved in determining the structure of the blue band is film thickness and that most of the peaks that we observe are due to optical interference effects.

#### 3.4. The influence of As on the growth of GaN films by MBE

Several studies have shown that the properties of GaN films grown by MBE depend critically on the growth conditions. Both growth temperature and the N-to-Ga ratio play crucial roles in determining quality of the GaN films, the electrical properties and the device performance [33–36]. Under N-rich growth conditions, columnar GaN films are obtained, but under more Ga-rich conditions the islands coalesce and, with excess Ga, one can obtain atomically smooth surfaces in between the Ga droplets. GaN films with optimum electrical properties are achieved in the intermediate regime, before the formation of Ga droplets [35, 36]. The width of this intermediate regime is finite and dependent on the growth temperature, increasing with increasing temperature.

Surfactants can have a significant influence on the properties of III–V compounds grown both by MBE and by MOVPE. We have shown that for GaN films grown by MBE, arsenic has a very significant influence on the morphology of the films [26]. An arsenic flux changes the surface reconstruction observed during growth and also improves the root mean square



**Figure 5.** AFM images of the surface morphology of films grown without ((a), (b)) and with arsenic ((c), (d)). The rms roughnesses for the samples are: (a) 18.10 nm, (b) 10.91 nm, (c) 4.62 nm and (d) 10.35 nm.

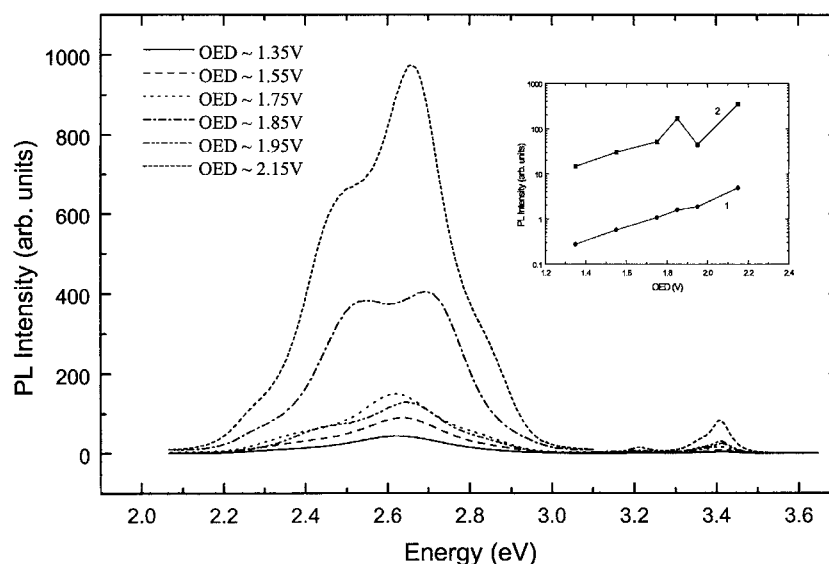
(rms) roughness of the films as measured by AFM. At low arsenic fluxes, large flat islands with atomic steps are observed, but with increasing arsenic flux the surface becomes rougher.

To study the influence of arsenic on the nitrogen-to-gallium ratio required to obtain optimum morphology and optical properties for GaN films grown by MBE, two sets of samples were grown under identical conditions with and without arsenic.

Figure 5 shows AFM images for the two sets of samples, grown with and without an arsenic flux for the same N-to-Ga ratio. For the films grown without arsenic, it is well known that there is an optimum III/V ratio for smooth films [35,36]. In our case the best morphology is obtained for an OED value of 1.75, as shown in figure 5(a). However, with a small increase in the N flux the films become columnar, as shown in figure 5(b). By contrast, for films grown with an arsenic flux present for the same Ga and N fluxes, instead of a transition to columnar growth, we observe an increase in the size of the subgrains, as shown in figures 5(c) and (d).

The room temperature PL from the set of films grown without an intentional arsenic flux depends strongly on the Ga:N ratio. At the lowest N-to-Ga ratio, the band edge emission at 3.4 eV is relatively weak, but as we approach stoichiometric growth, by increasing the amount of active nitrogen to the optimum OED value (for the OED, see the experimental details), the intensity of the band edge emission increases to a maximum value. At the point where the morphology changes from a flat terrace structure to columnar growth (figures 5(a) to (b)), the intensity of the band edge luminescence starts to decrease. At the highest N-to-Ga ratio, no PL is detected at room temperature. At the same time, we also see significant differences in





**Figure 6.** Dependences of the PL intensity for GaN films grown by MBE at 800 °C with different active nitrogen fluxes as measured using the OED. The inset shows the dependence of the band edge emission at 3.4 eV (1) and the blue emission at 2.6 eV (2) on the OED value.

the deep emission above and below the optimum OED value. This may indicate that there are different types of defect level introduced under Ga- and N-rich growth conditions. However, the important point is that the strongest band edge PL at room temperature is obtained in films grown under slightly gallium-rich conditions; this is similar to the situation for optimum transport properties where the highest mobilities are also obtained under slightly Ga-rich conditions [35, 36].

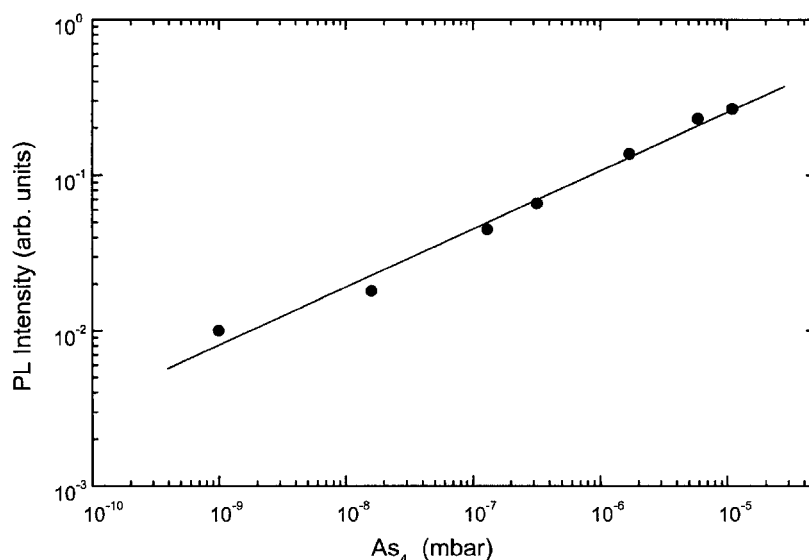
A quite different behaviour is observed for films grown with arsenic. As shown in figure 6, with increasing N-to-Ga ratio, there is a monotonic increase in the intensities of both the band edge emission at about 3.4 eV and the blue emission at about 2.6 eV. We see an increase in the intensity of the blue emission of more than one order of magnitude for a relatively small change in the flux of active nitrogen. We also observe a similar increase in the intensity of the band edge emission. This indicates that the two optical recombination processes may be related. Contrary to the situation without arsenic, we see a progressive increase in intensity over the whole range of Ga:N ratios which we have studied.

Our results suggests that arsenic has a strong influence on the optimum growth conditions for GaN films, changing the growth kinetics, the surface morphology, the optical properties and the nature of the electrically active defects.

### 3.5. PL at ~3.2 eV in As-doped GaN

In the presence of arsenic, in addition to the band edge emission at 3.4 eV we see an additional peak at 3.2 eV. The nature of this peak is still under investigation. It may be related to cubic GaN or to a donor-acceptor pair recombination process.

In previous studies of the growth of GaN on (100)-oriented cubic GaAs or GaP substrates, we observed that the presence of arsenic promoted the growth of cubic (zinc-blende) GaN, epitaxially related to the substrate, and suppressed the growth of hexagonal (wurtzite) GaN [18]. As a result we observed a decrease in the intensity of the band edge emission at 3.4 eV and



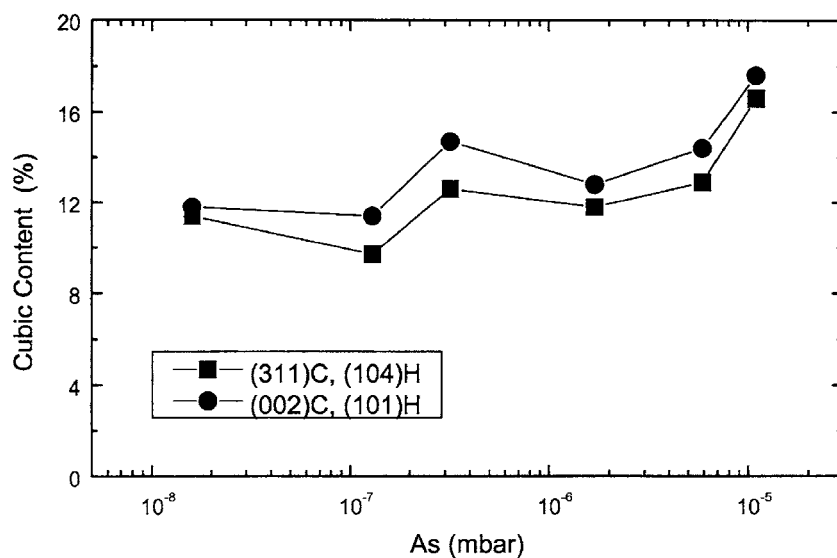
**Figure 7.** The dependence of the intensity of the PL emission at 3.2 eV on the arsenic flux used during growth by MBE.

a corresponding increase in the intensity of the band edge emission at 3.2 eV. However, it is well known that there are other possible optical transitions in wurtzite GaN, which give rise to a peak at 3.2 eV [31].

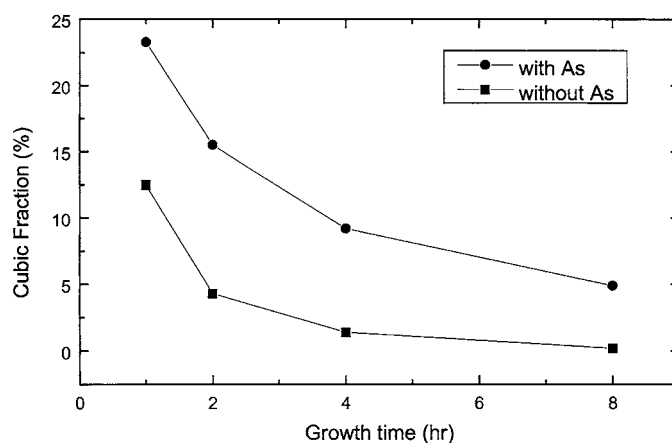
Figure 7 shows the intensity of the PL emission at 3.2 eV as a function of arsenic flux for samples grown with As<sub>4</sub>. A similar dependence is observed for samples grown with As<sub>2</sub>, but the power dependence may be slightly different. With changing N-to-Ga ratio, however, we see an initial increase in intensity of the peak at 3.2 eV and at a certain N-to-Ga ratio the intensity then decreases abruptly.

To investigate the origin of this peak we carried out x-ray diffraction studies of the cubic/hexagonal content in the films. To estimate the cubic content of the films we compared the intensities of cubic and hexagonal reflections, taking into account the various factors needed to obtain a reliable quantitative estimate of the cubic/hexagonal ratio. Two sets of reflections have been used to calculate the cubic content. The intensity of the 311 cubic peak has been compared with that of the 10 $\bar{1}$ 4 hexagonal peak and the 002 cubic reflection has been measured relative to the 10 $\bar{1}$ 1 hexagonal reflection. These sets of reflections are chosen to have common angles of incidence. The results of this study are shown in figure 8. It can be seen that the cubic fraction is small and does not increase strongly with the arsenic flux. For any given sample the calculated cubic contents for the two sets of reflections are the same within experimental error. Overall, however, the variation in cubic fraction is small compared with the change in the intensity of the PL peak at 3.2 eV. It is clear, therefore, that the cubic content and the PL peak intensity at 3.2 eV are not strongly correlated.

We have studied the cubic contents of samples grown with and without arsenic as a function of sample thickness. The results of this study are shown in figure 9. The cubic fraction decreases monotonically with increasing film thickness, consistent with there being an initial film of finite thickness with a fixed cubic-to-hexagonal GaN ratio, but for As-doped films there remains a small cubic fraction throughout the film, at least to the thickness studied. Electron-hole recombination in this cubic phase GaN could be responsible for the UV peak observed in PL at 3.2 eV, but the fraction of cubic phase GaN does not change significantly with



**Figure 8.** Dependences of the cubic contents of the films determined by x-ray diffraction studies on the arsenic flux during growth by MBE.

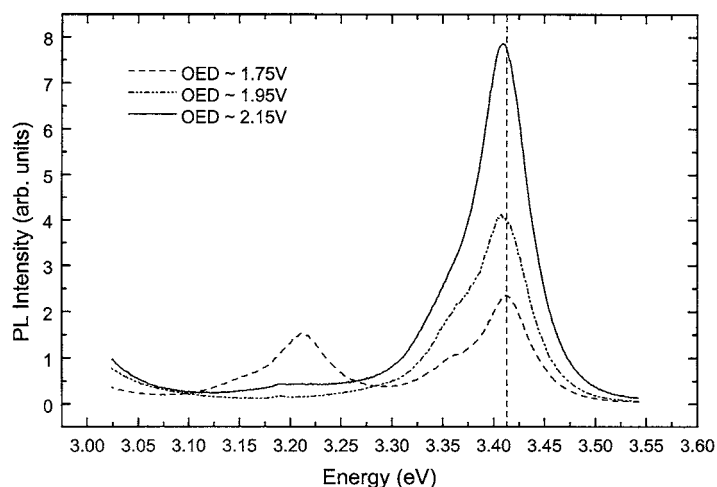


**Figure 9.** The dependence of the cubic content determined by x-ray diffraction studies on film thickness for both undoped and arsenic-doped layers grown by MBE.

As flux, whereas the PL intensity does. This suggests that the UV peak at 3.2 eV may be in part associated with donor–acceptor pair recombination as has previously been observed [31]. The nature of this transition is still under investigation.

### 3.6. The transition from blue emission in As-doped GaN to GaNAs alloys in layers grown by molecular beam epitaxy

GaN<sub>1-x</sub>As<sub>x</sub> alloys at the GaN-rich end of the phase diagram have been grown by both MBE [17, 24] and by MOVPE [15, 20]. For both techniques, it is difficult to obtain high concentrations of As in the alloy before phase separation occurs. The maximum concentrations



**Figure 10.** Near-band-edge PL spectra for arsenic-doped GaN films grown by MBE with different active nitrogen fluxes as measured using the OED.

in MBE layers reported to date are  $x \sim 0.26\%$  [17] for films grown at  $750^\circ\text{C}$  and  $x \sim 1\%$  [24] for films grown at  $500^\circ\text{C}$  respectively; this suggests that the solubility limit may be a function of temperature.

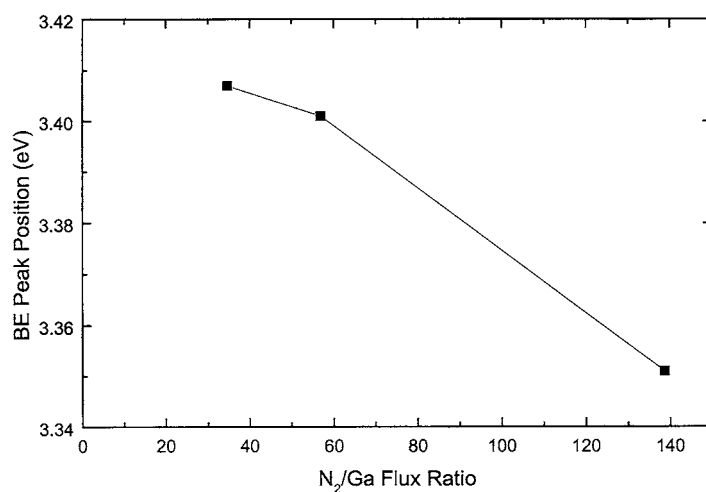
In previous studies of the growth of GaN:As films by MBE and MOVPE, only blue emission or  $\text{GaN}_{1-x}\text{As}_x$  alloy formation has been reported, but the transition between the two has not been understood.

As discussed above, we have studied the influence of changing the N/Ga ratio on the optical properties of the films. In the first studies we kept the Ga and As fluxes constant and changed the amount of active nitrogen. However, this method only allows us to change the ratio by a relatively small amount due to the limited dynamic range of the plasma source. In a second case, we kept the As and N fluxes constant and varied the Ga flux over a wide range.

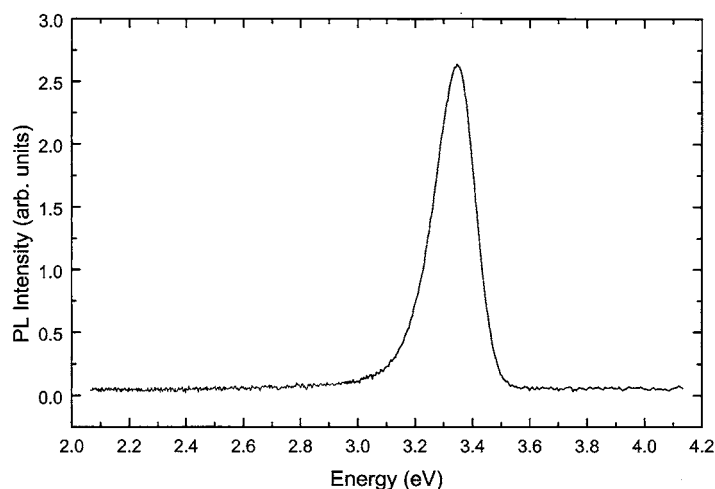
Using the first method, we have studied the influence of changing the N/Ga ratio on the formation of  $\text{GaN}_{1-x}\text{As}_x$  alloys during growth by MBE. As shown in figure 6 and confirmed for additional samples shown in figure 10, with increasing N-to-Ga ratio, three effects are observed. The intensity of the blue emission increases, the peak at 3.2 eV disappears at the highest N-to-Ga ratio and the position of the band edge peak shifts to lower energy. This shift may be due to the formation of an alloy, but might also be due to residual strain in the films introduced by arsenic.

To investigate this in more detail, we have used the second method to give larger variations in the N:Ga ratio by changing the Ga flux. As shown in figure 11, increasing the N/Ga ratio by this method leads to a much larger red-shift in the position of the band edge emission. As shown in figure 12, under N-rich conditions the PL spectrum changes completely. All evidence for blue emission disappears and we are left with a broad peak which is shifted to low energy, as compared to undoped GaN.

The observation that we need to have a high N/Ga flux ratio to promote the growth of the alloy is at first sight surprising. With increasing N/Ga ratio, we might expect to increase the density of Ga vacancies in the lattice and thus increase the possibility of incorporating As on the Ga sublattice as predicted theoretically [6]. Theoretically, conditions of greater N enrichment are predicted to raise the formation energy of  $\text{As}_\text{N}$  and lower the formation



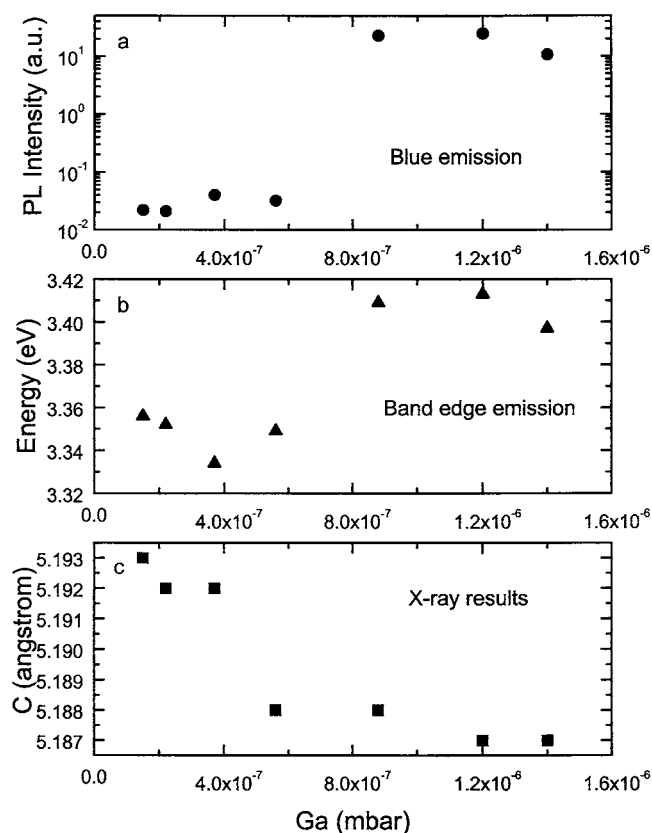
**Figure 11.** Band edge peak energy for GaNAs films grown by MBE with different Ga fluxes used to change the N/Ga ratio.



**Figure 12.** A typical PL spectrum for a  $GaN_{1-x}As_x$  alloy film grown with a high N/Ga flux ratio.

energy of  $As_{Ga}$  [6], which is directly contrary to our observation that we need nitrogen-rich conditions to form the alloy.

Figure 13 shows the variation in the intensity of the blue emission, the position of the band edge emission and the lattice parameter of the layers as a function of Ga flux. It is evident that for all three quantities there are two regions of Ga flux. At high Ga fluxes, the band edge and blue emission intensities are strong, the position of the band edge emission and the lattice parameter of the layers are close to the values for undoped GaN. On the other hand, at lower Ga fluxes the intensities of the band edge and blue emission decrease by several orders of magnitude for blue emission and by an order of magnitude for the band edge emission. At the same time we observe a significant shift in the position of the band edge emission to lower energy and a change in the lattice parameter indicating the formation of



**Figure 13.** Dependences of the blue emission intensity at 2.6 eV (a), the position of the band edge emission (b) and the lattice parameter of the GaNAs films (c) as a function of the Ga flux used during MBE growth.

a GaN<sub>1-x</sub>As<sub>x</sub> alloy with a significant arsenic content. Finally, it is important to recognize that the two effects are related: as the blue emission decreases, the alloy formation takes place.

The most likely explanation for this shift in band edge emission and change in lattice parameter is the formation of a GaN<sub>1-x</sub>As<sub>x</sub> alloy. From this shift in energy, using theoretical predictions of the band gap bowing in this alloy system [1], we can estimate the As mole fraction in the GaN<sub>1-x</sub>As<sub>x</sub> alloy to be  $x \sim 0.2\%$ . From the change in lattice parameter, assuming Vegard's law, we can also estimate the alloy content to be approximately the same. For growth at 800 °C, this is similar to the maximum concentration previously reported at 750 °C [17].

As already shown in figures 10 and 11, there is a progressive shift in the energy of the band edge emission with increasing N/Ga ratio. This suggests that for a constant arsenic flux, with increasing N/Ga ratio, i.e. growth under increasingly more nitrogen-rich conditions, the alloy composition changes from  $x \sim 0$  to 0.2%. In figure 13, the change in the N:Ga ratio is somewhat larger and this gradual change is not so obvious, but, combining all the sets of data, it is evident that the transition occurs over a finite range of N:Ga flux ratio. Thus, contrary to theoretical predictions [6], we find that, in order to form an alloy of GaN<sub>1-x</sub>As<sub>x</sub>, we need to have a high nitrogen-to-gallium flux ratio.

We can suggest several possible models to explain this surprising result based on previous studies of GaN growth kinetics. There is now good evidence that under Ga-rich conditions a thin layer of Ga (1–3 monolayers) exists on the surface during growth, but under N-rich conditions this probably does not exist. Under very Ga-rich conditions, Ga droplets are commonly observed on the surface [35, 36]. Our data support the hypothesis that to obtain GaN films showing strong blue emission you need this excess Ga on the surface during growth, but to grow  $\text{GaN}_{1-x}\text{As}_x$  alloys it is essential to increase the N:Ga ratio, which avoids the presence of excess Ga on the surface. The absence or presence of excess Ga may in turn lead to several possible models consistent with our data. Firstly, we may propose that under Ga-rich or N-rich conditions we grow films of opposite polarity and that the incorporation of As in each polarity will differ. A second possible model is that the rate of incorporation of impurities and the stoichiometry of the GaN will be influenced by the monolayers of Ga present on the surface. Under Ga-rich conditions, growth occurs via a liquid–solid interface, but under nitrogen-rich conditions growth takes place at a vapour–solid boundary.

An alternative explanation may be based on the idea that the mechanisms controlling alloy growth are similar to those in other III–V materials. Under such conditions, from thermodynamic considerations we might expect to have significant concentrations of Ga and N vacancies at the growth temperature. As predicted theoretically [6], due to the fact that arsenic and gallium atoms are similar in size, some authors suggest that arsenic atoms will initially try to occupy the vacancies on the Ga sublattice, producing blue emission. With increasing N/Ga ratio we may expect to increase the number of Ga vacancies at high temperature and therefore initially increase the density of arsenic atoms on the Ga sublattice, thus increasing the intensity of the blue emission at 2.6 eV. When the solubility limit for arsenic on the Ga sublattice is reached, further increases in the N/Ga ratio must either result in arsenic being incorporated onto the N sublattice or cause phase separation into As-doped GaN and N-doped GaAs. However, as we have demonstrated experimentally, increasing the N/Ga ratio reduces the tendency to phase separation and therefore the additional As is incorporated onto the N sublattice, promoting the growth of the alloy. It is also possible that, during cooling, arsenic, which is initially on the Ga sublattice, will form a  $\text{GaN}_{1-x}\text{As}_x$  alloy. It is evident that the real process is more complicated than this simple model and additional theoretical and experimental data are required to fully understand this behaviour.

#### 4. Summary and conclusions

We have studied the growth and properties of GaN:As layers prepared by MBE. We have demonstrated that arsenic doping during growth produces films showing blue emission at room temperature. The blue emission is centred at 2.6 eV and is more than a decade stronger than the band edge emission. The blue emission is strong enough to be clearly visible under normal room lighting. Similar results are observed with arsenic in the form of dimers or tetramers. The intensity of the blue emission depends very strongly on the arsenic content in the films. The blue emission peak is broad and in thick films shows structure due to thickness oscillations. The morphology of GaN is influenced strongly by the presence of arsenic. The intensities of both band edge emission at 3.4 eV and blue emission at 2.6 eV from arsenic-doped films is strongly influenced by the N-to-Ga flux ratio during growth by MBE. The nature of the band edge peak at 3.2 eV, which is observed for arsenic-doped films of GaN, is still not resolved. With increasing N-to-Ga flux ratio during growth by MBE, we observe a transition from films which show blue emission at 2.6 eV to films which show  $\text{GaN}_{1-x}\text{As}_x$  alloy formation. Arsenic doping of GaN during growth by MBE influences directly both the morphology of the films and their electrical and optical properties; such layers have great potential for future device applications.

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