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# CATHODOLUMINESCENCE FROM GALLIUM NITRIDE IMPLANTED WITH ARSENIC OR PHOSPHORUS

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Phosphorus and arsenic impurities have been introduced into single crystal thin films of gallium nitride by ion implantation. New luminescence bands are observed at 2.85 eV for the phosphorus implant and at 2.58 eV for the arsenic implant. There is some evidence for charge carrier compensation. A band at 2.2 eV is associated with implantation damage and high temperature annealing.

## 1. Introduction

Gallium nitride is a III–V semiconductor with a wurtzite structure. It has a high direct band gap, 3.50 eV at 1.6 K [1,2,3], and has been the subject of extensive investigation as a possible material for the construction of light emitting devices to extend the range of colours available from current light emitting diodes [4–7].

The most successful growth techniques use vapour transport [5,6,7], and yield n-type material. Electron concentrations normally lie within the range from $10^{17}$ $cm^{-3}$ to $10^{20}$ $cm^{-3}$, and the residual donor is thought to be the nitrogen vacancy [8]. Insulating material has been grown by compensating the donors with group I or group IIB impurities [9–15], leading to the construction of MIS-type light emitting diodes. Attempts to grow p-type material have been unsuccessful. Possible reasons for this are over-compensation by the native donors and the formation of complex centres with other impurities or defect. Acceptor dopants do in fact form deep complexes [13–17] and these are the effective compensators in the growth of insulating material.

Diffusion coefficients of impurities in GaN are low [18] so that doping is normally carried out by including the impurities in the source chemicals of the growth process. Ion implantation is an alternative technique with which impurity concentrations that are well above normal chemical equilibrium values are obtained. It has been used to implant Zn into GaN [19,20,21]; the damage in the implanted layer quenches luminescence, but this can be recovered by high temperature annealing.

This paper describes the effect of the implantation of possible isoelectronic group V impurities, phosphorus and arsenic, upon the luminescence from GaN.

## 2. Experiment

### (a) *Preparation of samples*

GaN was grown in the form of epitaxial layers with $(21\bar{3}1)$ orientation on $(11\bar{2}0)$ sapphire substrates by the vapour transport method described by Wickenden et al. [22].

Single crystal layers were formed, about 10 $\mu$m thick and 1 cm square. They were transparent throughout the visible spectrum, but showed slip bands parallel to the basal plane introduced by thermal stress between the sample and the substrate on cooling.

Each sample was cut into four parts. One was reserved for electrical conductivity measurements by the Van der Pauw technique, and as a reference in luminescence measurements. The sample used for P implantation had an initial electron concentration of $4.0 \times 10^{19}$ cm$^{-3}$ at room temperature, and the sample used for As implantation had an initial electron concentration of $3.4 \times 10^{19}$ cm$^{-3}$.

### (b) *Implantation*

Ion implantation was carried out with a Danfysic 98000 machine. P and As were introduced into the source chamber as $P_2O_5$ and $As_2S_3$ vapour and were ionised by a helical beam of electrons. The $P^+$ or $As^+$ ions were selected by a mass spectrometer and accelerated onto the GaN layers. The beam was inclined at 7° to the normal to the GaN layers to prevent channeling along preferred crystallographic directions. The samples were at room temperature.

On the theory of Lindhardt, Scharff, and Schiott [21] the concentration $N_x$ of an implanted species follows a Gaussian profile with the depth of penetration $x$, given by:

$$N_x = N_0 \exp -\left\{\frac{(x - R_p)^2}{2\Delta R_p^2}\right\},$$

where $R_p$ is the mean projected range and $\Delta R_p$ the standard deviation in $R_p$. The values of $R_p$ and $\Delta R_p$ depend on the incident ion energy, and on the mass and atomic number of the implanted and target atoms. Table 1 summarises the implantation data calculated from information given by Dearnaly [21]. The maximum accelerating potential in the system was 82 kV, and this was used for the $As^+$ ions, giving a mean projected range of 23 nm. The lighter $P^+$ ions were accelerated to give the same mean projected range. The ion flux rates were varied for each specimen, to

Table 1
Implantation data calculated from reference [21]

| Implanted ion | Initial electron concentration in unimplanted samples $n$ ($cm^{-3}$) | Implanted ion energy $E$ (keV) | Mean projected range $R_p$ (nm) | Standard deviation $\Delta R_p$ (nm) | Calculated peak concentrations $N_0$ ($cm^{-3}$) | | |
|---|---|---|---|---|---|---|---|
| $P^+$ | $4 \times 10^{19}$ | 40 | 23 | 11 | $1.6 \times 10^{20}$ | $1.6 \times 10^{19}$ | $1.6 \times 10^{18}$ |
| $As^+$ | $3.4 \times 10^{19}$ | 82 | 23 | 9.5 | $1.1 \times 10^{20}$ | $1.1 \times 10^{19}$ | $1.1 \times 10^{18}$ |

give $N_0$ values spanning the initial electron concentrations in each sample. Implantation data calculated from [21] are given in table 1.

*(c) Annealing*

Each nuclear collision produces a knocked on target atom, which in turn produces a cascade of secondary collisions, giving rise to a small, highly damaged volume which may be amorphous in nature [22,23]. However, much of the damage appears to be removed by self-annealing, assisted by charges trapped at defect centres [21]. LEED measurements on GaN implanted with $Zn^+$ at similar energies show no evidence of amorphous material [24] and it is assumed that some crystalline order is preserved. However, residual damage is still high enough to quench luminescence, which is recovered by annealing at elevated temperatures in $NH_3$ to prevent N loss from the GaN [8].

*(d) Cathodoluminescence (CL)*

Luminescence was excited by an electron beam from an electrostatically focused GEC T984 electron gun giving accelerating potentials within the range from 8 kV to 20 kV. The sample was mounted on the cold finger of an Oxford Instruments CF 100 continuous flow cryostat with conducting silver paste. The sample chamber was kept at pressures below $10^{-5}$ Torr. Temperatures down to 8 K could be achieved with liquid helium and 73 K with liquid nitrogen. Temperatures were monitored on an Oxford Instruments CLTS resistance thermometer and could be held steady at ±0.1 K between 8 K and 40 K and ±2 K from 40 K to 300 K, using an Oxford Instruments PID temperature controller. Measurements were made at 8 kV, with a beam current of 300 nA on a spot size of 0.5 mm diameter, or at 15 kV giving a beam current of 1 μA on a 0.5 mm spot.

Electron beam penetration in solids follows an approximate dependence of the

form [25]

$$R_x = 8.5 \times 10^{-2} E^{3/2}/\rho,$$

where $R_x$ = projected maximum range in $\mu$m
$E$ = electron beam energy in keV
$\rho$ = target density in g cm$^{-3}$,
which gives

$$R_x \cong 0.3\ \mu\text{m at 8 keV},$$

and

$$R_x \cong 1.0\ \mu\text{m at 15 keV}.$$

The region in which luminescence is excited by the electron beam is determined by the energy loss from the incident beam, and the diffusion of the excess charge carriers produced by the beam. The maximum rate of energy loss from the beam occurs at about a half of the projected maximum range. Diffusion of the excess charge carriers from this region before recombination increases the range of depths from which luminescence originates. The diffusion lengths of excess carriers in the implanted layers and sub-layers are not known, but taking typical values of about 0.6 $\mu$m for holes in n-type GaAs at electron concentrations of $3 \times 10^{18}$ cm$^{-3}$ [26] as a basis for argument it would appear that a large part of the luminescence generated by the 8 kV beam should originate within the implanted layer, with some contribution from the GaN below the implanted layer, but the relative contribution from the implanted layer should drop significantly for the 15 kV beam.

The spectra were analysed and recorded using a Barr and Stroud VL1 monochromator with quartz prisms. This has a reciprocal dispersion at the exit slit of 0.25 mm/nm at 360 nm and 0.05 mm/nm at 720 nm. Preliminary measurements had indicated the broad nature of the luminescence features, and the slits were set to an energy band width of 30 meV at 360 nm to allow for adequate light intensities at the EMI 9558 Q photomultiplier.

The detection and monochromator system was calibrated for intensity response over the required spectral range with a standardised tungsten filament lamp. The results for various slit widths were incorporated into a general correction programme which was applied to the recorded spectra.

The intensity of luminescence varied with the position of the beam on the sample, and areas of maximum luminescence efficiency were selected for the measurements, by a preliminary scan over each sample.

## 3. Luminescence results

### (a) *Undoped GaN*

The unimplanted GaN specimens gave CL spectra which were dominated by two features identified by previous workers.

(i) The A-band, which occurs between 3.4 and 3.5 eV and has been associated with band to band recombination. The observed bands showed the same properties as those reported previously [27] with peak energies depending on the penetration of the Fermi level into the conduction band, and decreasing with increasing temperature, following the energy gap decrease.

(ii) The B-band, extending from 3.3 eV into the visible range. At low carrier concentrations it has been identified with donor–acceptor pair recombination, but at higher carrier concentrations where the donor levels are degenerate with the conduction band a conduction band to acceptor level transition has been proposed [16]. As the carrier concentration increases the relative strength of the A to B band increases, and this effect is illustrated in fig. 1. B-bands are rapidly quenched at temperatures above 80 K, and are not observed at room temperature.

The sharp peaks below 2 eV have been identified as impurity luminescence from the sapphire substrates.

*(b) Phosphorus implanted GaN*

Figure 2 shows CL spectra from GaN:P samples at 77 K, after post implantation annealing at 900°C. A previously unreported feature appears as a clearly resolved band at 2.85 eV in the $\sim 10^{19}$ cm$^{-3}$ and $\sim 10^{20}$ cm$^{-3}$ implants and as a low energy

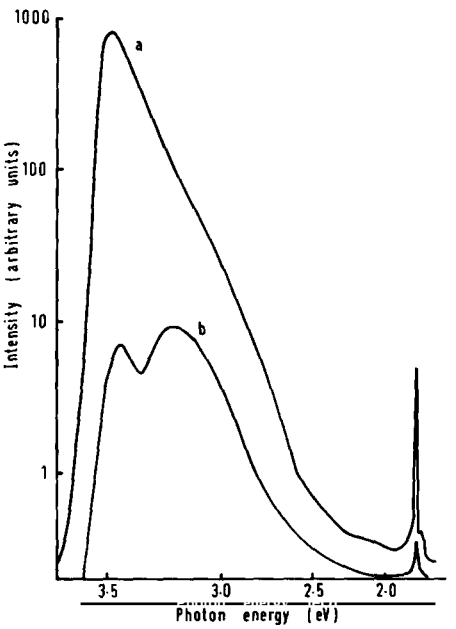


Fig. 1. Unimplanted GaN. Cathodoluminescence at 77 K. Electron energy 15 keV. (a) carrier concentration = $3.4 \times 10^{19}$ cm$^{-3}$; (b) carrier concentration = $1.1 \times 10^{19}$ cm$^{-3}$.

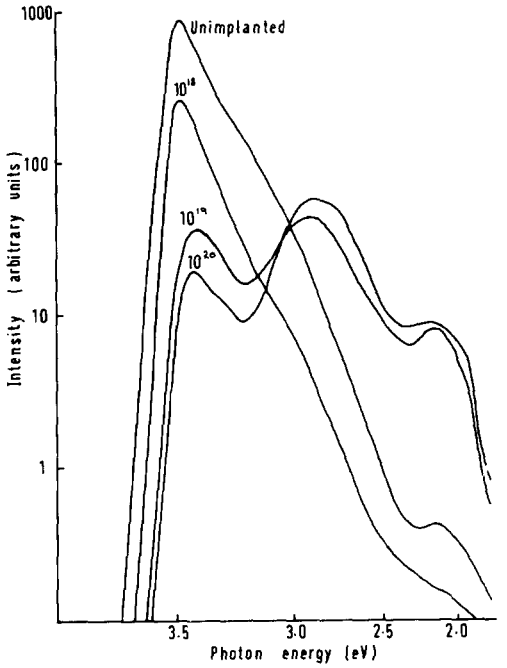


Fig. 2. Cathodoluminescence of P implanted samples at 77 K. Electron energy = 8 keV, annealing temperature = 900°C.

shoulder in the $\sim 10^{18}$ $cm^{-3}$ implants. A yellow band at 2.2 eV is also obtained. The A bands have shifted to lower energies than those of the unimplanted material and appear to be less intense. At 294 K (fig. 3) the 2.85 eV band is resolved in the $\sim 10^{19}$ $cm^{-3}$ and $\sim 10^{20}$ $cm^{-3}$ implants. No significant shift of peak energy with temperature is observed for this band. Intensities are lower than for the 77 K spectra.

Figure 4 shows the dependence of the CL spectra on electron beam energy at 73 K. At the higher energy, the A band increases in intensity, the 2.85 eV band to a lesser extent, and the 2.2 eV shows no significant change.

The development of the luminescence was followed through the post-implantation annealing process. The samples were annealed at 600°C for 6 hours, 745°C for 30 minutes, 770°C for 30 minutes, 900°C for 15 minutes, 920°C for 15 minutes and 930°C for 15 minutes. Luminescence spectra were taken after each anneal. The 2.85 eV and 2.2 eV bands were first observed after the 745°C anneal, and their intensity relative to the A-band increased at each anneal up to 900°C. Above this temperature the relative intensity of the 2.85 eV band decreased, but that of the 2.2 eV band increased.

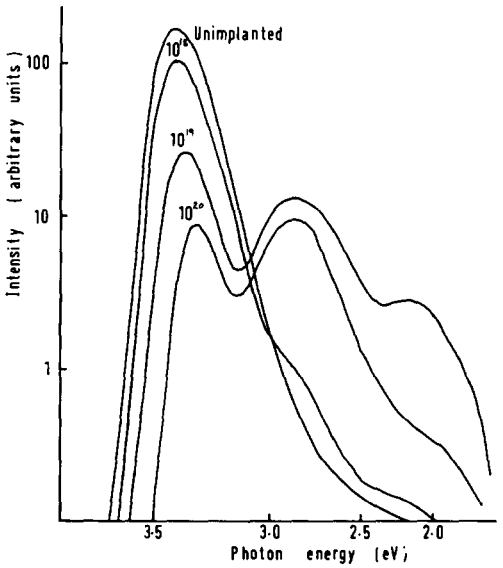


Fig. 3. Cathodoluminescence of P implanted samples at 294 K. Electron energy = 8 keV, annealing temperature = 900°C.

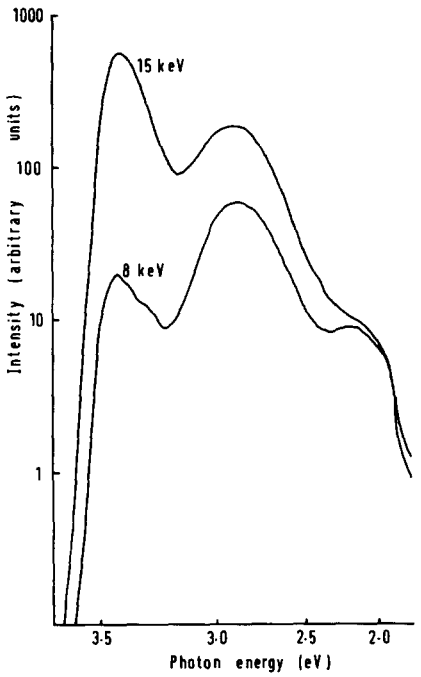


Fig. 4. Cathodoluminescence of P implanted ($10^{20}$ $cm^{-3}$) samples at 73 K. Annealing temperature = 900°C.

### (c) *Arsenic implanted GaN*

Figure 5 shows CL spectra from GaN : As samples at 73 K annealed to 900°C. A new band appears at 2.58 eV. The A-band intensity decreases with increasing ion dose and the B-band becomes resolved. The 2.2 eV emission appears as a low energy shoulder on the 2.58 eV band. At 295 K (fig. 6) the new band shifts to a peak energy of 2.53 eV and its intensity relative to the A-band decreases. The intensities observed from this band are generally weaker than those observed for the new band in the GaN : P samples.

The A band luminescence increases in intensity with beam energy, and the B band is no longer resolved. The new band at 2.58 eV increases in intensity, but its intensity relative to the A band falls (fig. 7).

The annealing history of these samples is slightly different from the GaN : P samples, but further experiments have indicated that the differences are not significant. Samples were annealed at 600°C for 6 hours, 745°C for 15 minutes, 770°C for 15 minutes, 900°C for 15 minutes, 920°C for 15 minutes and 930°C for 15 minutes. The 2.58 eV band appeared after annealing at 900°C and the 2.2 eV shoulder at 745°C. Annealing above 900°C caused a decrease in the intensities of the B-band and the 2.58 eV band relative to the A band, but the 2.2 eV increased in intensity and was resolved from the 2.58 eV band.

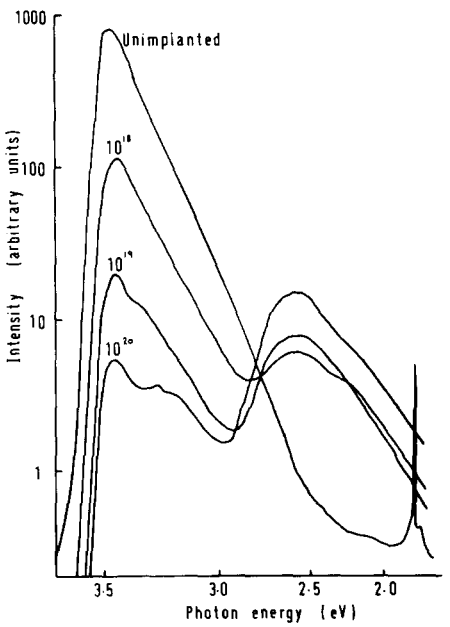


Fig. 5. Cathodoluminescence of As implanted samples at 73 K. Electron energy = 8 keV, annealing temperature = 900°C.

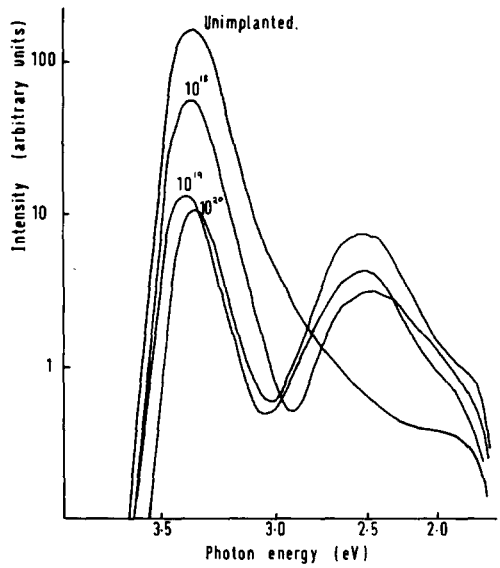


Fig. 6. Cathodoluminescence of As implanted samples at 295 K. Electron energy = 8 keV, annealing temperature = 900°C.

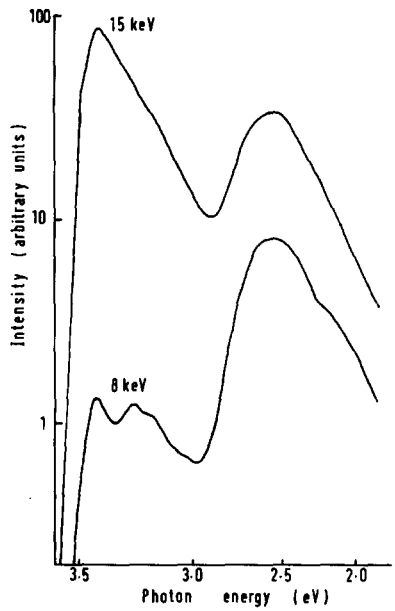


Fig. 7. Cathodoluminescence of As implanted ($10^{20}$ $cm^{-3}$) samples at 73 K. Annealing temperature = 900°C.

## 4. Discussion

This work is part of a general programme studying the luminescence from a wide range of ion-implanted impurities in GaN. The CL bands near 2.53 eV and 2.85 eV only appeared with implanted $As^+$ and $P^+$ impurities respectively, and must be associated with the presence of these impurities in the system. However, these preliminary experimental results do not allow a detailed description of the nature of the impurity centres or the radiative transitions. The energies indicate impurity levels about 1.0 and 0.65 eV from the band edges, rather than the shallow isoelectronic traps observed in GaP for example [28]. The undoped samples have high A-band to B-band ratios; this is normal in material with high initial electron concentrations, and the ratio is often taken as an approximate indication of the electron concentration. There is a noticeable reduction in the ratio for the GaN : As material, indicating a significant reduction in the electron concentration with the impurity centres acting as compensating centres. However, the reduction of the A-band intensity because of competing non-radiative transitions at residual damage centres is another possibility which is supported by an approximate proportionality between the initial damage and the reduction in the A-band intensity.

The evidence for carrier compensation in GaN : P is inconclusive although the luminescence of the 2.85 eV band is strong. This band appears at lower annealing temperatures than the GaN : As band, and disappears more rapidly on annealing above 900°C. The smaller phosphorus ions could be more mobile and cause less lattice strain than the arsenic ions, leading to out-diffusion at higher annealing temperatures.

The half-widths and temperature dependences of these two group V bands are similar to that of a 2.89 eV band obtained from zinc implanted GaN grown by the same process [19]. It has been suggested that the zinc bands are due to tunnelling-assisted conduction band to acceptor transitions, but more detailed work upon the lifetime and temperature dependences of these Group V bands is required before any detailed description could be given to their mechanism.

The 2.2 eV band is associated with initial damage caused by ion implantation and with high temperature annealing. It is located nearer the surface (i.e. excited by lower energy electrons) than the impurity emission. It appears in all implanted and annealed material, and in some unimplanted samples after high temperature annealing, and could be associated with defects formed during high temperature dissociation of GaN.

During the preparation of this paper, new results from Pankove and Hutchby [30] of photoluminescence from a wide range of ion implanted GaN samples became available. The results on samples doped with As and P show substantial agreement with our cathodoluminescence results.

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