

A study of annealed GaN grown by molecular beam epitaxy using photoluminescence spectroscopy.

Abigail Bell^{1,2}, Ian Harrison², Dimitris Korakakis^{1,2}, Eric C. Larkins², J. M. Hayes³, M. Kuball³.

¹School of Physics and Astronomy, University of Nottingham, Nottingham, NG7 2RD, UK

²School of Electrical and Electronic Engineering, University of Nottingham, Nottingham, NG7 2RD, UK.

³H.H.Wills Physics Laboratory, University of Bristol, Bristol, BS8 1TL, UK

ABSTRACT

Photoluminescence (PL) spectroscopy has been used to investigate the effect annealing has on molecular beam epitaxially grown GaN in different ambients. By observing the changes in the PL spectra as a function of ambient temperature and atmosphere used, important information concerning the origin of defects within GaN has been found. Samples were annealed in different atmospheres, (including oxygen, oxygen and water vapour, nitrogen and argon), different temperatures. In the 2.0eV-2.8eV region of the PL spectra, two peaks appeared at approximately 2.3eV and 2.6eV, somewhat higher than the usual yellow luminescence peak. We find that the 2.6eV peak is dominant for high annealing temperatures and the 2.3eV peak dominates at low annealing temperatures for the samples annealed in oxygen. When annealed in argon and nitrogen the 2.6eV peak dominates at all annealing temperatures. Changes in the PL spectra between anneals were also seen in the 3.42eV region. The 3.42eV peak is often assigned to excitons bound to stacking faults. Power resolved measurements indicate that in our sample the cause is a donor acceptor pair transition.

INTRODUCTION

Group-III nitrides are direct, wide band gap semiconductors and have many potential uses in optoelectronic devices. The optical and electrical properties of these materials are affected not only by the processes that occur during growth, but also by the post-growth processes that the material undergoes, such as thermal annealing. Photoluminescence (PL) is used widely to characterise the nitrides. It gives a good indication of the radiative processes that occur within the material. Non-radiative paths reduce the intensity of the PL peaks and so PL is a good indicator of the optical quality of the material. The origins of many of the peaks that commonly occur in GaN are still not clear. One such peak is the so-called “yellow luminescence” which is a broad peak that appears in the PL spectra at approximately 2.2eV. *Ogino and Aoki* [1] describe the transition as occurring between a shallow donor 25meV below the conduction band and an acceptor 860meV above the valence band. *Glaser et al* [2] performed PL and optically detected magnetic resonance (ODMR) on GaN layers. They suggested it is a two-part transition in which there is a non-radiative capture between a shallow and deep-donor state followed by a radiative transition between the deep-donor state and a shallow acceptor (possibly C on a N site). *Ponce et al* [3] suggested that the sources of the yellow emission are either dislocations at low angle grain boundaries in the material or point

defects, which nucleate at dislocations. It has also been suggested by *Reynolds et al* [4], that the yellow band in GaN results from a transition between a shallow donor and a deep level. The deep level in the Reynolds's model was attributed to a complex consisting of a Ga vacancy and oxygen on a nitrogen site ($V_{\text{Ga}}\text{-O}_{\text{N}}$). Another commonly occurring peak in GaN is the 3.427eV peak, seen in the 4K PL spectra. It was initially attributed to oxygen forming a shallow "deep level"[5]. However, it has more recently been suggested that peaks in the PL spectra of GaN in this region 3.40eV [6-8], 3.412eV [9] and 3.42eV [10] can be related to excitons bound to stacking faults.

By annealing samples of GaN in different ambients and at different temperatures, we have clarified some of the issues regarding the role that defects play, particularly in the "yellow luminescence" and the near 3.42eV luminescence regions. GaN samples grown by MBE have been used in this study and annealed at different temperatures in oxygen, oxygen plus water vapour, nitrogen, nitrogen plus water vapour and argon in a high-temperature stage.

EXPERIMENTAL METHOD

The layer used in this work (sample MG671) was grown by MBE in a modified Varian Mod Gen II machine. The active nitrogen was produced by radio-frequency (RF) plasma source and the Ga was produced from solid elemental sources. The sample was an unintentionally doped 1 μm thick GaN layer grown on a (0001) sapphire substrate. Grown on top of the GaN was a high-mobility field effect transistor (FET) structure consisting of 3nm undoped $\text{Al}_{0.15}\text{Ga}_{0.85}\text{N}/22\text{nm}$ Si-doped $\text{Al}_{0.15}\text{Ga}_{0.85}\text{N}/15\text{nm}$ undoped $\text{Al}_{0.15}\text{Ga}_{0.85}\text{N}$. Pieces of the sample MG671 were annealed for 20mins using a high temperature stage at various temperatures and in various gases. The pieces of MG671 were labelled numerically and will be referred to as (number) in the remainder of the paper. The annealing details and sample numbers are shown in table 1.

The photoluminescence spectra were taken using a 325nm CW HeCd laser with a maximum excitation intensity of 9mW. A 325nm band pass filter was used to attenuate lines other than the 325nm laser line. A quartz lens focused the beam onto the sample in a liquid helium cryostat. The excitation light was normal to the sample and the resulting PL was focused through a low-pass sharp cut-off filter (Oriel WG345), used to stop the laser light, onto the monochromator slit. The 0.75m Spex monochromator, with a 2400 lines/mm grating, has a resolution of 4 \AA /mm, which correspond to 4meV/mm in the region of 3.4eV. The light was detected by a bi-alkali photomultiplier (Thorn 9924QB) with a 600V applied voltage. Standard phase sensitive detection techniques were used to improve the signal to noise ratio.

Table 1. Sample numbers with annealing parameters.

Temperature ($^{\circ}\text{C}$)	800	900	1000	1100	1200
O_2	40	41	41	44	
O_2 and H_2O			63		
N_2			9	46	7
N_2 and H_2O			61		
Ar			16	18	19
Pre-annealed	39				

RESULTS

In all of the 4K PL spectra (figure 1) there is a peak which occurs in the region from 3.467eV to 3.479eV and it has been attributed to the donor bound exciton (D^0X) [11]. In addition, a peak appears at approximately 3.40eV-3.42eV in all of the spectra. Transitions in this region are commonly attributed to an exciton bound to a stacking fault [6-10]. There is no clear consensus to the exact energy at which this occurs (3.40eV [6-8], 3.412eV [9], 3.42eV[10]). From figure 1, the peaks in this area are more pronounced after annealing at higher temperatures (42,44) and in a water vapour atmosphere (63). There also appears to be a correlation between the strain [12], as determined by the position of the D^0X peak and the intensity of the 3.42eV peak, which could support the stacking fault hypothesis. To investigate this further we have performed power resolved measurements since the excitonic transition should not shift with power. The results are shown in figure 2 for the sample annealed in an atmosphere of H_2O and O_2 (63). In this case the peaks at 3.418eV and 3.36eV shift to higher energy with increasing excitation intensity. If the stacking faults act as quantum wells as described in the literature you might also expect to see a blue shift with increasing excitation intensity. However an alternative explanation for the blueshift is that the 3.42eV peak is a DAP transition[13]. A similar transition has been seen by *Eunsoon et al* [14]. The samples annealed in N_2 and Ar exhibit a peak in this region which also blueshifts with increasing excitation intensity (not shown here). Although in the case of the N_2 annealed samples, the peak only appears when annealed above 1100°C.

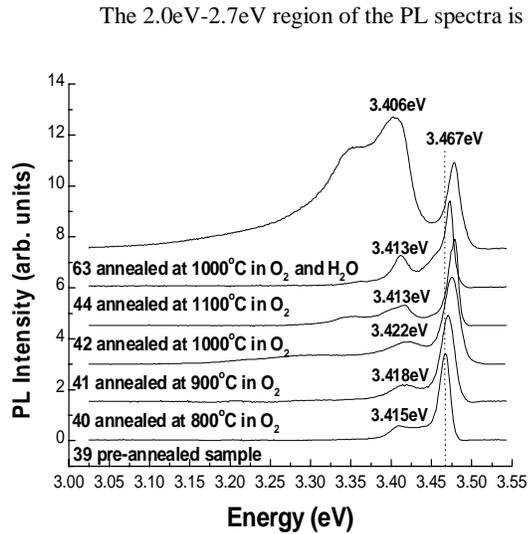


Figure 1. 4K PL spectra of sample annealed in O_2 and H_2O at different temperatures. The position of the D^0X peak shifts from 3.467eV to higher energy after annealing.

The 2.0eV-2.7eV region of the PL spectra is considerably altered by annealing the sample. Figure 3 shows the room temperature PL spectra between 2.0eV-3.1eV of the pre-annealed (39), annealed in O_2 (40, 41, 42, 44) and annealed in O_2 and H_2O (63) samples. The pre-annealed sample (39) exhibits only weak PL in this region, with peaks at 2.3eV and 2.6eV, where the intensity of the 2.6eV peak dominates. This is at a somewhat higher energy than the usual “yellow luminescence” found in GaN between 2.0-2.2eV [1-4]. Annealing the samples in O_2 greatly enhances the PL intensity at 2.3eV and 2.6eV, although increasing the annealing temperature to above 1100°C causes the 2.6eV peak intensity to

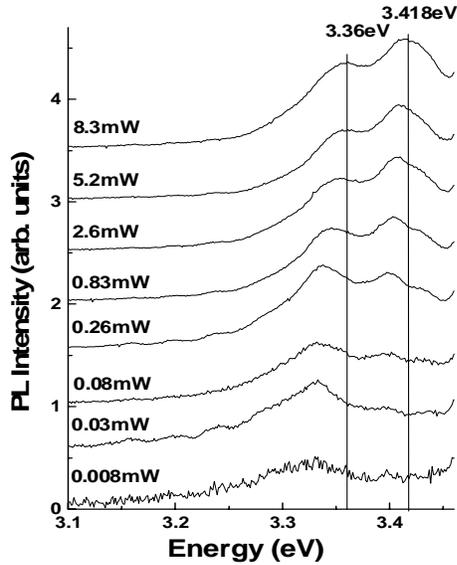


Figure 2. Power resolved PL of sample 63 annealed in O_2 and H_2O at $1000^\circ C$. The $3.418eV$ and $3.36eV$ peaks shifts with excitation intensity, typical of a DAP transition. The D^0X peak, not shown here, is at $3.479eV$ and does not shift.

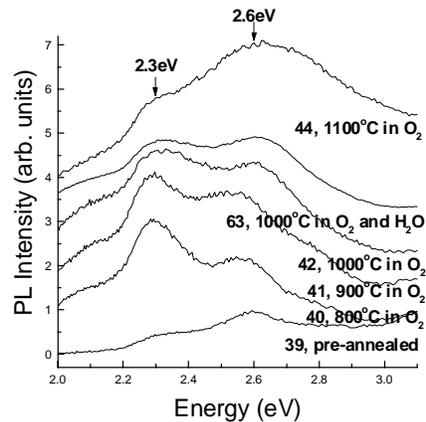


Figure 3. 300K PL spectra of samples annealed in O_2 or O_2 plus H_2O at different temperatures. Peaks at $2.3eV$ and $2.6eV$, shown with an arrow, become stronger upon annealing in O_2 , this effect is even stronger when annealing in O_2 and H_2O .

become even greater than the $2.3eV$ peak. Annealing in both O_2 and H_2O increases the intensity of both the $2.3eV$ and $2.6eV$ peaks. The two arrows on figure 3 are guides for the eye to the $2.3eV$ and $2.6eV$ PL peaks. Calculations were made and it was found that both the $2.3eV$ and $2.6eV$ peaks are real PL peaks and not Fabry-Perot thickness oscillations. Similar PL spectra were obtained from the samples annealed in N_2 and Ar, although the $2.6eV$ peak is dominant (spectra not shown here). The PL intensity in this region in the N_2 and Ar annealed samples also increases with increasing annealing temperature.

Figure 4 shows the power resolved PL of the sample annealed in O_2 and H_2O (63) in the $2.0eV$ to $3.1eV$ region. The $2.3eV$ peak shifts to a higher energy with increasing excitation intensity indicating that it may be DAP type recombination. However, the $2.6eV$ peak does not appear to shift over two decades of excitation power and so has free-bound character. The $2.6eV$ and $2.3eV$ peaks often occur together. If we assume that there is a common defect in these two transitions then we can have two possible situations shown in figure 5a and 5b. When the samples were annealed in O_2 both peaks increased in intensity. However, when the samples were annealed in N_2 and Ar,

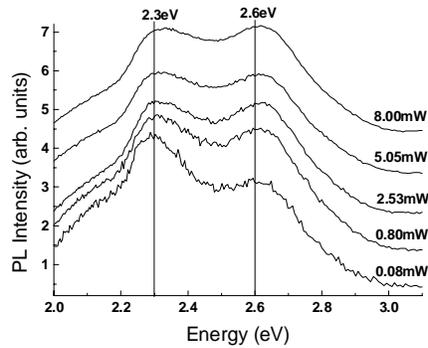


Figure 4. Power resolved PL of sample 63 annealed at 1000°C in O₂ and H₂O. As the excitation intensity is increased the 2.3eV peak shifts to a higher energy suggesting a DAP transition. There is no such shift of the 2.6eV peak.

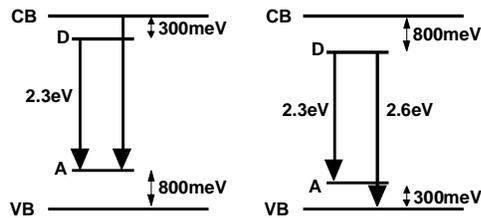


Figure 5(a) A deep acceptor takes part in recombination from an electron on a shallow donor and the conduction band. (b) A deep donor level carries electrons that recombine with both a shallow acceptor level and the valence band.

stacking faults as suggested in the literature [6-10], this would suggest that annealing our material introduces stacking faults and that at higher annealing temperatures, more stacking faults are introduced into the sample. However, an alternative explanation that the 3.42eV peak is DAP in nature is offered. The increase in the intensity of this line with annealing can then be attributed to the increase in defect (donor or acceptor) concentration.

Deep levels were introduced into the samples by annealing them in various atmospheres. This deep level luminescence consisted of two peaks at 2.3eV and 2.6eV, which is considerably higher in energy than the usual “yellow luminescence” seen in GaN between 2.0eV -2.2eV. In all of the samples, annealing increased the deep level luminescence and increasing the annealing temperature further enhanced the PL intensities. The 2.3eV peak is a DAP transition, as determined from power resolved PL. The near

the 2.6eV peak was dominant suggesting that the annealing process introduces the deep acceptor. The increase in the 2.3eV DAP transition in the O₂ annealed samples provides evidence for the donor at 300meV being oxygen related. However, it is important to remember that if the model 5b had been used, these arguments would point to an oxygen related acceptor. When H₂O was introduced into the anneal, both peak intensities were increased. This would suggest that the addition of water somehow enhances the introduction of donors (or acceptors) as discussed previously.

CONCLUSIONS

Annealing the material introduces a defect causing a transition at approximately 3.42eV. A peak appears in this region independent of the annealing atmosphere, although its intensity increases with annealing temperature. If this emission is related to

2.6eV peak was dominant in the Ar and N₂ annealed samples. In the samples annealed in oxygen, both peaks competed. suggesting that the 2.3eV peak is related to oxygen. Two possible models have been suggested and outlined for this luminescence. These models consist of the free-to-bound and DAP transitions being due to either the same donor or acceptor.

ACKNOWLEDGEMENTS

We would like to acknowledge the EPSRC Blue UV laser diode program and the EU BRITE EURAM MIGHT project No BE98-4899 for part funding on this work. AB would also like to thank the University of Nottingham for her studentship. The work in Bristol was in part sponsored by Renishaw plc. (Dr. G. D. Pitt)

REFERENCES

- [1] T.Ogino and M.Aoki, *Jpn.J.Appl.Phys.* **19** p2395 (1980)
- [2] E.R.Glaser, T.A.Kennedy, K.Doverspike, L.B.Rowland, D.K.Gaskill, J.A.Freitas Jr, M.Asif Khan, D.T.Olsen, J.N.Kuznia and D.K.Wickenden, *Phys.Rev.B* **51** p13326 (1995)
- [3] F.A.Ponce, D.P.Bour, W.Gotz and P.J.Wright, *Appl.Phys.Lett.* **68** p57 (1996)
- [4] D.C.Reynolds, D.C.Look, B.Jogai, J.E.Van Norstrand, R.Jones and J.Jenny, *Solid State Commun.*, **106** p701 (1998)
- [5] B-C Chung and M Gershenzon, *J.Appl.Phys.* **72** p651 (1992)
- [6] M.Albrecht, S.Christiansen, G.Salviati, C.Zanotti-Fregonara, Y.T.Rebane, Y.G.Shreter, M.Mayer, A.Pelzmann, M.Kamp, K.J.Ebeling, M.D.Bremser, R.F.Davis and H.P.Strunk, *Mat.Res.Soc.Symp.Proc.Vol.468* p293 (1997)
- [7] Y.T.Rebane, Y.G.Shreter, and M.Albrecht, *Mat.Res.Soc.Symp.Proc.Vol.468* p179 (1997)
- [8] Y.T.Rebane, Y.G.Shreter, and M.Albrecht, *phys.stat.sol.(a)* **164** 141 1997
- [9] S.Fischer, G.Steude, D.M.Hofmann, F.Kurth, F.Anders, M.Topf, B.K.Meyer, F.Bertram, M.Schmidt, J.Christen, L.Eckey, J.Holst, A.Hoffmann, B.Mensching, B.Rauschenbach, *J.Cryst.Growth* **189/190** p556 (1998)
- [10] G.Salviati, C.Zanotti-Fregonara, M.Albrecht, S.Christiansen, H.P.Strunk, M.Mayer, A.Pelzmann, M.Kamp, K.J.Ebeling, M.D.Bremser, R.F.Davis, Y.G.Shreter, *Inst.Phys.Conf.Ser.* **157** p199 (1997)
- [11] O.Lagerstedt and B.Monemar, *J.Appl.Phys.* **45** p2266 (1974)
- [12] J.M. Hayes, M. Kuball, A. Bell, I. Harrison, D. Korakakis, and C.T. Foxon, *Appl. Phys. Lett.* **75** p2097 (1999)
- [13] H.B.Bebb and E.W.Williams, *Semicond. Semimet.*, **8** p4-5 (1972)
- [14] Eunsoon Oh, Bonjin Kim, Hyeonsoo Park, and Yongjo Park, *Appl.Phys.Lett.* **73** p1883 (1998)