A3.3 Luminescence of GaN

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A INTRODUCTION

Luminescence in various forms (photo- (PL), cathodo- (CL) or electroluminescence (EL)) is a traditional, non-destructive technique for semiconductor characterisation. In this Datareview the most important luminescence transitions observed in undoped and doped GaN will be described.

B EDGE LUMINESCENCE OF UNDOPED α-GaN

As discussed in Datareviews A3.1 and A3.4, there exist large variations of strain state among GaN samples. For biaxial stress, shifts of the bandedge exciton energies at a rate of 23 meV/GPa [1] or 27 meV/GPa [2] have been reported. Though the ground state energy is not expected to vary linearly with strain, such variations appear to be valid in a wide range [1-3]. Another difficulty is that doping or non-stoichiometry can induce a hydrostatic component in the stress [2]. As such, a first step for the interpretation of the luminescence spectra of GaN should be the measurement of the excitonic gap of the sample. A straightforward method is to cross-check luminescence with reflectivity measurements. Indeed, well resolved transitions from the A, B and C free excitons (i.e. involving holes from the Γ_9, Γ_{7upper} and Γ_{7lower} valence bands, respectively) can easily be observed in high quality undoped GaN [3-7], allowing a precise determination of their energies. Another approach to discriminating free versus bound excitons is to perform temperature dependent luminescence experiments, since for T ranging between 50 and 100 K, bound excitons are thermally delocalised to the benefit of free excitonic recombination [7-9]. FIGURE 1 displays the typical near edge luminescence spectra of unintentionally doped GaN as a function of temperature, in order to discuss the various spectral features observed in high purity GaN. At low T ($T \leq 10$ K), the luminescence spectra of GaN are dominated either by bound exciton [3-7] (see FIGURE 1), or free exciton recombinations [9-11] (see also FIGURE 2). The dominant bound exciton line lies typically 6 ± 0.5 meV lower in energy than the free A exciton recombination. Since undoped GaN is always grown n-type, this transition is ascribed to neutral donor bound exciton recombination. It is often labelled I_2, following the notation of Dingle et al [4], or D^0X. The I_2 line is weakly replicated by LO phonons, 91.5 meV lower in energy. Whereas most reports indicate a single donor bound exciton line, in some cases at least two transitions can be resolved, assigned to the presence of distinct donors [12-15]. The binding energy E_b of a donor bound exciton is approximately given, following Haynes rule, by $E_b = 0.2\ E_D$ where E_D is the donor binding energy [14].

As mentioned previously, FIGURE 1 shows that the bound exciton line is thermally quenched when the temperature rises and, for $T \geq 100$ K, the spectra are dominated by free A excitons. The A exciton is strongly replicated by LO phonons. The theoretical line shape of the free exciton LO replica is $I(E) \propto E^{3/2}\exp(-E/kT)$ for the one LO replica and $I(E) \propto E^{1/2}\exp(-E/kT)$ for the 2 LO replica [16]. This was verified at moderate temperature by Kovalev et al [17]. The intensity ratio of the one LO- and two LO-replicas varies linearly with T [8]. According to their line shape, the separation between the luminescence of the A exciton and of its phonon replica is less than the LO phonon energy, and decreases with T [18], as shown in FIGURE 1. At room temperature, most reports indicate that the luminescence spectrum of undoped GaN is dominated by free A exciton recombination [8,11,19], as can be checked by reflectivity. However, for the sake of completeness, recent arguments in favour of band to band luminescence dominating at 300 K are also presented [20].

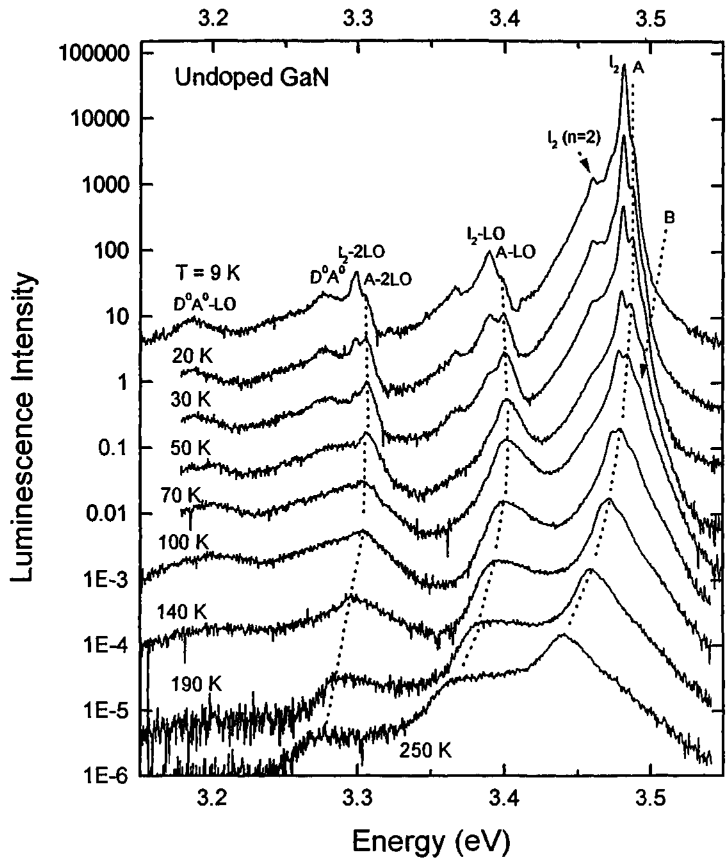

FIGURE 1 Typical temperature dependence of the edge PL spectrum of undoped GaN (sample grown on (0001) sapphire by MOVPE). Each spectrum has been shifted by half a decade for clarity of the figure.

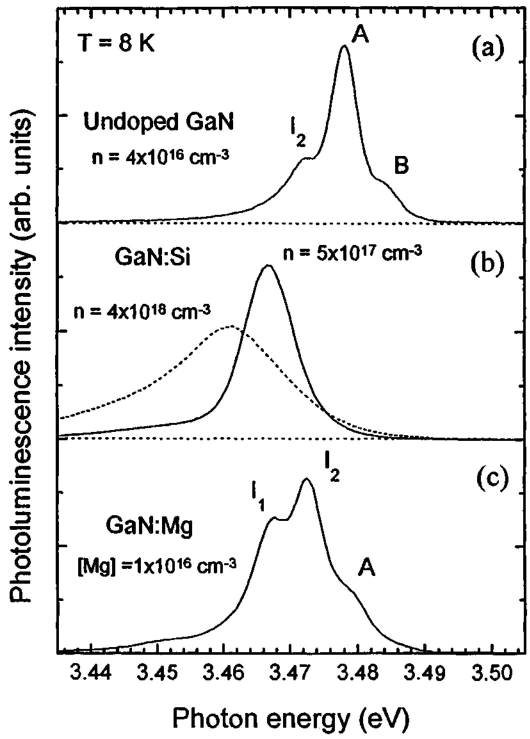

FIGURE 2 10 K luminescence in the excitonic energy range of undoped, Si-doped and slightly Mg-doped GaN. The samples are grown by MBE on (0001) sapphire. After [35].

On increasing the temperature, B and even C free excitons are thermally populated and their contribution can be observed in the bandedge luminescence of undoped GaN (see FIGURE 1). At helium temperature weak luminescence peaks located 19 - 20 meV higher in energy than the A line [6,13,19,21] are frequently observed. Their attribution to n = 2 states of the A exciton can be used to evaluate the A Rydberg. Doing so leads to values of 25 ± 2 meV.

Another feature clearly observed in FIGURE 1 is the sharp transition on the low energy side of the I_2 line and labelled I_2 (n = 2). It is interpreted as a two electron satellite of the donor bound exciton line, i.e. due to a recombination where the donor is left in its n = 2 excited state [6,19]. From the 22 ± 0.5 meV separation from the I_2 line, a donor binding energy of 29 ± 1 meV can be deduced [6,19]. The weak transitions in FIGURE 1 at 3.27 and 3.18 eV, attributed to donor-acceptor pair recombinations, are discussed below.

C DEFECT-RELATED LUMINESCENCE

In this section we will discuss transitions frequently observed in undoped GaN which are generally not related to bandedge or shallow level recombination. The first is the so-called yellow band. This wide band, peaking at 2.2 ± 0.1 eV, is almost systematically observed in undoped or n-type GaN. An important study of this transition was performed by Ogino and Aoki [22] who concluded that it involves transitions between free or weakly bound electrons and an 860 meV deep acceptor. Their experiments (high temperature luminescence and absorption) were interpreted in the context of a level strongly coupled to the lattice ($S\hbar\omega \approx 13 \times 41$ meV) that was attributed to a complex involving carbon presumably associated with a Ga vacancy [22]. Another interpretation of the yellow band as owing to transitions between a deep donor and a shallow acceptor was proposed by Glaser et al [23] on the basis of magnetic resonance experiments, but more recent reports favour the original deep acceptor model [24-26]. Chen et al associate this deep level with the N antisite (N_{Ga}) defect. From the theoretical point of view, the deep acceptor involved could be the Ga vacancy, possibly as a complex with a donor impurity such as oxygen [27] (this is close to the early interpretation by Ogino and Aoki [22]). The ratio between the yellow band and the bandedge luminescence intensities is often used as a figure of merit to assess the quality of GaN layers. As pointed out by Grieshaber et al [28], this ratio is highly dependent on the excitation intensity, and should be used as a standard with caution.

Another type of transition which is sometimes observed in heteroepitaxial GaN consists of a main band peaking in the 3.40 - 3.42 eV range. Various interpretations have been proposed. An early one, by Chung and Gershenzon [29], was that this band is due to the recombination of free holes with 78 meV deep donors, tentatively attributed to oxygen. It is however considered now that oxygen donors are not that deep in GaN. Another interpretation of transitions in this energy range in terms of donor-shallow (90 meV) acceptor pair recombination can be found in [30]. This comes from the temperature and excitation intensity dependence of the 3.40 - 3.42 eV band, which is also shown to be structured by sharp adjacent peaks [30]. It is to be noted that the intensity of the 3.40 - 3.42 eV luminescence is related to poor crystalline quality, as shown by its sensitivity to low temperature buffer layer growth [21], and to the fact that it originates mainly from the substrate epilayer interface [31,32]. As such, this defect luminescence is rather attributed to excitons bound to extended structural defects such as screw dislocations [31] or stacking faults [32]. In the latter case, the stacking fault is considered to behave as a type-II cubic quantum well in a hexagonal matrix [32]. Recently, Monemar [33] has suggested that the 3.40 - 3.42 eV luminescence could be LO assisted free carrier recombination in highly disordered material. Clearly, a final assignment of this defect luminescence is lacking. This 3.4 eV luminescence is accompanied by other transitions at lower energies [21,31,32].

D LUMINESCENCE OF n-DOPED α-GaN

GaN can easily be doped n-type (for instance by Si), and carrier densities up to the 10^{19} cm^{-3} range can be reproducibly obtained. Starting from undoped GaN with room temperature (RT) residual doping in the 10^{16} cm^{-3} range, the effect of a slight Si doping ($n < 10^{18}$ cm^{-3}) is to shift the bandedge luminescence towards low energy (see **FIGURE** 2). This is due in part to a decrease of the compressive stress in the sample due to Si doping [2,34], but also to a deepening of the main luminescence transition relative to the energy of A [19]. This last point can be related to either a broadening of the donor bound exciton band or to the emergence of free hole neutral donor recombinations [19]. For n doping higher than 10^{18} cm^{-3}, i.e. higher than the critical Mott density, the luminescence spectra of GaN display a large broadening, due to the formation of a broad low energy tail (see FIGURE 2), and, for $n > 10^{19}$ cm^{-3}, a blue shift of the high energy cut-off occurs. The increase of the width of the edge luminescence band roughly follows an $n^{2/3}$ law [19]. All these results seem to imply that the evolution with n-doping of the luminescence spectra is due to phase space filling effects. However, the width of the spectra is slightly lower than could be expected for indirect (in k space) transitions [19], as is the case for smaller gap semiconductors such as GaAs or InP. Similarly, Cunningham et al reported a Burstein shift smaller than expected for an electron mass of $0.2m_0$ [36]. It should also be noted that for $n > 10^{18}$ cm^{-3}, it is difficult to observe marked reflectance structures, i.e. to evaluate optically the strain of the sample. Lee et al [34] have shown that Si doping reduces the in-plane stress in GaN.

E LUMINESCENCE OF p-DOPED α-GaN

Pankove and Hutchby [37] early reported the luminescence of GaN implanted by thirty-five elements, including those expected to behave as acceptors. Apart from bandedge luminescence, PL maxima appear to be grouped around 3.2, 2.9, 2.5, 2.2 and 1.7 eV. Among the most studied acceptor impurities in GaN are Zn and Mg (the latter being the only element efficient in giving p-type conduction). Monemar et al [38] have studied by PL Zn-doped GaN, and they report PL peaks at 2.87, 2.6, 2.2 or 1.8 eV, dependent on doping level, with a moderate coupling to the lattice. The 2.87 eV band is related to substitutional Zn_{Ga}. The zero phonon peak at ≈3.1 eV requires a Zn acceptor depth of ≈370 meV [38]. This is in agreement with theoretical calculations [39]. The Zn bound exciton line was reported to be ≈34 meV lower in energy than the A line [14,40].

There have been numerous reports on the luminescence of Mg-doped GaN (e.g. [19,35,40-44, 46-49]). In samples that are weakly Mg-doped, Mg doping results in the appearance of a new bound exciton line, ≈11 meV lower in energy than the A free exciton (see FIGURE 2), and in an increase of the 3.27 eV donor-acceptor pairs band (FIGURES 1 and 3). This new bound exciton line, labelled I_1 in FIGURE 2, is often ascribed to neutral acceptor bound exciton recombination (I_1 or A^0X) [12,19,35,43]. Other authors ascribe it to ionised donor bound excitons (D^+X) [9], or to excitons bound to a deep neutral donor [14,15]. The coupling with LO phonons of the I_1 line is about ten times stronger than for the I_2 line, favouring its identification in terms of an acceptor bound exciton. Indeed, Wysmolek et al [42] relate this strong coupling to the existence of a neutral acceptor-LO phonon bound state. It appears that there is no consensus concerning the depth (relative to A) of the shallow (residual or Mg) acceptor bound exciton, and that binding energies of 11 meV [12,19,35,42], 14 - 16 meV [43] and 19 meV [4,40] have been quoted. FIGURE 3 displays the excitation intensity and temperature dependence of the shallow acceptor related transitions observed in weakly Mg-doped GaN. At low T, the slight red shift with decreasing excitation of the main band is typical of a donor acceptor pairs (D^0A^0) band, and this shift is consistent with an ≈220 - 225 meV deep acceptor and an ≈35 - 30 meV deep donor [44]. Similarly, the position of the free electron-neutral acceptor (eA^0) band appearing for T > 50 K, which is given by $E_g - E_A + kT/2$, leads to an acceptor depth of 220 - 225 meV [43,44]. This acceptor is often reported in the spectra of weakly Mg-doped GaN. It is worth pointing out that similar spectra can be observed for samples grown in machines where no magnesium has been used. This means either that Mg is the usual residual acceptor in GaN, or that the ≈220 meV deep acceptor is a more usual common impurity in III-V compounds. Carbon has been suggested as a pertinent candidate [44,45].

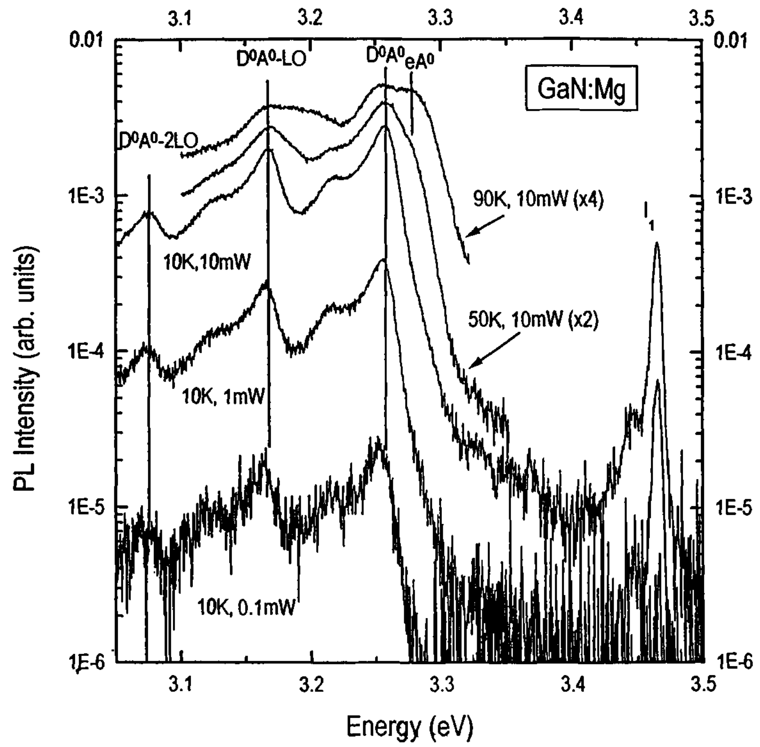

FIGURE 3 Excitation intensity and temperature dependence of the shallow acceptor related luminescence in slightly Mg-doped GaN. The sample is grown by MBE on (0001) sapphire.

At higher Mg doping (p ≈ 10^{17} cm^{-3} at 300 K, i.e. [Mg] ≈ 10^{19} cm^{-3}), a strong broadening of the PL spectra is observed, with peak energy at low temperature in the 2.8 - 2.9 eV or the 3.1 - 3.2 eV range, or both [19,35,40,46-49]. The 3.1 - 3.2 eV band is generally ascribed to free electron-Mg acceptor recombinations, from which an Mg depth of ≈270 - 290 meV was deduced [44,49] (this acceptor level is then different from the one discussed above). The origin of the deep blue band at 2.8 - 2.9 eV has been attributed to conduction band-deep Mg acceptor states or complexes recombination [49], to electron recombination with deep valence band tail states [46] or to recombinations between shallow bound holes and deep compensating donors [19]. Clearly, no definite answer can be given at the present stage. A final point to be noted is that, as in the case of high n-type doping, high p-type doping results in the disappearance of resolved reflectivity spectra, making difficult the optical evaluation of the strain level of highly Mg doped GaN samples.

F LUMINESCENCE OF β-GaN

There are many fewer reports on the luminescence of cubic GaN than on its hexagonal counterpart. Ramirez-Flores et al [50] studied the low temperature PL of cubic GaN on MgO substrates and reported donor-bound exciton recombination at 3.291 eV (11 meV lower in energy than the excitonic gap), and donor-acceptor pair recombination at 3.173 eV. Cubic GaN on (001) GaAs has been studied by Strite et al [51], As et al [52], Menniger et al [53,54] and Wu et al [55]. At low temperature, all these authors report bound exciton luminescence in the 3.268 ± 0.006 eV range and a donor acceptor pairs band in the 3.165 ± 0.015 eV range, pointing to a residual acceptor depth of about 130 meV. This value is much lower than the one found in α-GaN (see above) and is one of the promising features of cubic GaN relative to the hexagonal form. Menniger et al [53] report free exciton luminescence at 3.272 eV for α-GaN on GaAs, i.e. lower in energy than in α-GaN on MgO [50]. Low energy luminescence features at

3.08 eV [54,55] and 3.035 eV [55], observed in cubic GaN on GaAs, are ascribed to free electron-acceptor and donor-acceptor transitions involving a second, deeper (≈0.22 eV) residual acceptor.

G CONCLUSION

The band-edge luminescence of undoped, high quality α- and β-GaN is well mastered and is now a valuable characterisation tool, though the spectroscopy of β-GaN is not as mature as that of α-GaN. However, a clear understanding is still needed of the luminescence of deep levels, and of highly-doped GaN.

REFERENCES

[1] W.G. Perry, T. Zheleva, M.D. Bremser, R.F. Davies, W. Shan, J.J. Song [*J. Electron. Mater. (USA)* vol.26 (1997) p.224]
[2] C. Kieselowski et al [*Phys. Rev. B (USA)* vol.54 (1996) p.17745]
[3] B. Gil, O. Briot, R.L. Aulombard [*Phys. Rev. B (USA)* vol.52 (1995) p.R17028]
[4] R. Dingle, D.D. Sell, S.E. Stokowski, M. Ilegems [*Phys. Rev. B (USA)* vol. 4 (1971) p.1211]
[5] B. Monemar [*Phys. Rev. B (USA)* vol.10 (1974) p.676]
[6] B.J. Skromme et al [*Mater. Res. Soc. Symp. Proc. (USA)* vol.449 (1997) p.713]
[7] K. Pakula et al [*Solid State Commun. (USA)* vol.97 (1996) p.919]
[8] B. Monemar, J.P. Bergman, I.A. Buyanova, W. Li, H. Amano, I. Akasaki [*MRS Internet J. Nitride Semicond. Res. (USA)* vol.1 (1996) 2]
[9] B. Santic, C. Merz, U. Kaufmann, R. Niebuhr, H. Obloh, K. Bachem [*Appl. Phys. Lett. (USA)* vol.71 (1997) p.1837]
[10] W. Shan, T.J. Schmidt, X.H. Yang, J.J. Song, B. Goldenberg [*Appl. Phys. Lett. (USA)* vol.66 (1995) p.985]
[11] M. Tchounkeu, O. Briot, B. Gil, J.P. Alexis, R.L. Aulombard [*J. Appl. Phys. (USA)* vol.80 (1996) p.5352]
[12] H. Teisseyre et al [*MRS Internet J. Nitride Semicond. Res. (USA)* vol.1 (1996) 13]
[13] D. Volm et al [*Phys. Rev. B (USA)* vol.53 (1996) p.16543]
[14] B.K. Meyer [*Mater. Res. Soc. Symp. Proc. (USA)* vol.449 (1997) p.497]
[15] S. Fisher et al [*Mater. Sci. Eng. B (Switzerland)* vol.43 (1997) p.192]
[16] S. Permogorov [*Excitons* Eds. E.I.Rashba, M.D.Sturge (North Holland Publishing Company, New York, USA, 1982) p.177]; C.F. Klingshirm [*Semiconductor Optics* (Springer, Berlin, Germany, 1995) p.191]
[17] D. Kovalev, B. Averboukh, D. Volm, B.K. Meyer, H. Amano, I. Akasaki [*Phys. Rev. B (USA)* vol.54 (1996) p.2518]
[18] H.B. Bebb, E.W. Williams [*Semicond. Semimet. (USA)* vol.8 (1972) p.181]
[19] M. Leroux et al [*Mater. Sci. Eng. B (Switzerland)* vol.50 (1997) p.97]
[20] M. Smith, J.Y. Lin, H.X. Jiang, M.Asif Khan [*Appl. Phys. Lett. (USA)* vol.71 (1997) p.635]
[21] N. Grandjean, M. Leroux, M. Laügt, J. Massies [*Appl. Phys. Lett. (USA)* vol.71 (1997) p.240]
[22] T. Ogino, M. Aoki [*Jpn. J. Appl. Phys. (Japan)* vol.19 (1980) p.2395]
[23] E.R. Glaser et al [*Phys. Rev. B (USA)* vol.51 (1995) p.13326]
[24] D.M.Hoffman et al [*Phys. Rev. B (USA)* vol.52 (1995) p.16702]
[25] E. Calleja et al [*Phys. Rev. B (USA)* vol.55 (1997) p.4689]
[26] H.M. Chen, Y.F. Chen, M.C. Lee, M.S. Feng [*Phys. Rev. B (USA)* vol.56 (1997) p.6942]
[27] C.G. Van de Walle, J. Neugebauer [*Mater. Res. Soc. Symp. Proc. (USA)* vol.449 (1997) p.861]
[28] W. Grieshaber, E.F. Schubert, I.D. Goepfert, R.F. Karlicek, M.J. Schuman, C. Tran [*J. Appl. Phys. (USA)* vol.80 (1996) p.4615]

[29] B.-C. Chung, M. Gershenzon [*J. Appl. Phys. (USA)* vol.72 (1992) p.651]

[30] G.B. Ren, D.J. Dewsnip, D.E. Lacklison, J.W. Orton, T.S. Cheng, C.T. Foxon [*Mater. Sci. Eng. B (Switzerland)* vol.43 (1997) p.242]

[31] Y.G. Shreter et al [*Mater. Res. Soc. Symp. Proc. (USA)* vol.449 (1997) p.683]

[32] M. Albrecht et al [*Mater. Res. Soc. Symp. Proc. (USA)* vol.468 (1997) p.293]

[33] B. Monemar [*Proc. Int. Conf. Silicon Carbide and III-Nitrides* Stockholm, Sweden, 1997, to be published]

[34] I.H. Lee, I.H. Choi, C.R. Lee, S.K. Noh [*Appl. Phys. Lett (USA)* vol.71 (1997) p.1359]

[35] N. Grandjean, J. Massies, M. Leroux, P. Lorenzini [*Appl. Phys. Lett. (USA)* vol.72 (1997) p.82]

[36] R.D. Cunningham, R.W. Brander, N.D. Knee, D.K. Wickenden [*J. Lumin. (Netherlands)* vol.5 (1972) p.21]

[37] J.I. Pankove, J.A. Hutchby [*J. Appl. Phys. (USA)* vol.47 (1976) p.5387]

[38] B. Monemar, O. Lagerstedt, H.P. Gislason [*J. Appl. Phys. (USA)* vol.51 (1980) p.625]

[39] F. Bernardini, V. Fiorentini, R.M. Niemenen [*Proc. 23rd Int. Conf. Physics of Semiconductors* Eds. M. Scheffler, R. Zimmermann (World Scientific, 1996) p.2881]

[40] C. Merz, M. Kunzer, U. Kaufmann, I. Akasaki, H. Amano [*Semicond. Sci. Technol. (UK)* vol.11 (1996) p.712]

[41] S. Nakamura, G. Fasol [*The Blue Laser Diode* (Springer, Germany, 1997) p.79]

[42] A. Wysmolek, P. Lomiak, J.M. Baranowski, K. Pakula, R. Stepniewski, K.P. Korona [*Acta Physica Polon. (Poland)* vol.90 (1996) p.981]

[43] M.A.L. Johnson et al [*Mater. Res. Soc. Symp. Proc. (USA)* vol.449 (1997) p.215]

[44] M. Leroux, B. Beaumont, N. Grandjean, P. Gibart, J. Massies, J.P. Faurie [*MRS Internet J. Nitride Semicond. Res. (USA)* vol.1 (1996) 25]

[45] S. Fisher, C. Wetzel, E.E. Haller, B.K. Meyer [*Appl. Phys. Lett. (USA)* vol.67 (1995) p.1298]

[46] E. Oh, H. Park, Y. Park [*Appl. Phys. Lett. (USA)* vol.72 (1998) p.70]

[47] W. Götz, N.M. Johnson, J. Walker, D.P. Bour, R.A. Street [*Appl. Phys. Lett. (USA)* vol.68 (1996) p.667]

[48] M. Ilegems, R. Dingle [*J. Appl. Phys. (USA)* vol.44 (1973) p.4234]

[49] M. Smith et al [*Appl. Phys. Lett. (USA)* vol.68 (1996) p.1883]

[50] G. Ramirez-Flores, H. Navarro-Contreras, A. Lastras-Martinez, R.C. Powell, J.E. Greene [*Phys. Rev. B (USA)* vol.50 (1995) p.8433]

[51] S. Strite et al [*J. Vac. Sci. Technol. B (USA)* vol.9 (1991) p.1924]

[52] D.J. As, F. Schmilgus, C. Wang, B. Schöttker, D. Schikora, K. Lischka [*Appl. Phys. Lett. (USA)* vol.70 (1997) p.13311]

[53] J. Menniger, U. Jahn, O. Brandt, H. Yang, K. Ploog [*Phys. Rev. B (USA)* vol.53 (1996) p.1881]

[54] J. Menniger, U. Jahn, O. Brandt, H. Yang, K. Ploog [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.836]

[55] J. Wu, H. Yaguchi, K. Onabe, R. Ito, Y. Shiraki [*Appl. Phys. Lett. (USA)* vol.71 (1997) p.2067]