

Reactive-ion-etched gallium nitride: Metastable defects and yellow luminescence

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Gallium nitride has been reactive-ion etched with SF₆ and argon plasmas. The Ar-etched samples show a striking transition from a dominant blue luminescence band to a dominant yellow luminescence band after less than 5 min of low power illumination. The observation of metastable defects which are associated with *both* the yellow and blue bands has important consequences for our understanding of defect-related luminescence in gallium nitride. © 1999 American Institute of Physics. [S0003-6951(99)00747-0]

Gallium nitride (GaN) is a wide band gap semiconductor with a tremendous range of possible applications. It has a direct band gap of ~ 3.5 eV which makes it suitable for blue light emitting devices, including light emitting diodes and laser diodes.¹ A great deal of attention has been focused on the study of defects in GaN because of their potential to control device properties. However, an outstanding problem is that there is currently no generally accepted understanding of the defect-related yellow luminescence. Various models have been proposed²⁻⁹ but none seems to account for *all* the available data.

Reactive ion etching (RIE) is an important tool for device fabrication. We have previously developed a successful RIE process for GaN based on a SF₆ plasma.¹⁰ Although both donors and acceptors were introduced we have shown that our process does not destroy the band edge photoluminescence (PL)—this is a necessary condition for fabrication of efficient optical devices. In this letter we report on below band gap PL from GaN after RIE using SF₆ and argon plasmas. Under illumination with ultraviolet (UV) laser light the below band gap PL from the etched samples exhibits a dramatic shift from a dominant blue luminescence (BL) band to a dominant yellow luminescence (YL) band, i.e., metastable defects are created. The clear link between the YL and BL bands provides a new test for theories of the YL.

Our samples are 2.5- μm -thick nominally undoped GaN, grown by metalorganic vapor phase epitaxy on *c*-plane sapphire substrates. Our previous studies¹⁰ focused on the use of SF₆ as an etching gas with a power density of 0.45 W/cm², pressure 15 mTorr, and flow rate 40 sccm, resulting in a direct current (dc) bias of -440 V. In this work we compare a sample etched for 2.5 min in the SF₆ plasma at -440 V [labeled SF₆ (440 V)] with two samples etched for 2.5 min in an argon plasma under conditions resulting in dc biases of -440 V [Ar (440 V)] and -78 V [Ar (78 V)], and an unetched sample. Since the dc bias controls the energy of the

ions impacting on the GaN, and the argon plasma is believed to be inert, we are able to control and investigate the relative importance of the chemical etching and physical bombardment mechanisms that are intrinsic to the RIE process.

The experimental arrangements are similar to those in our previous work.¹⁰ One difference is that a Spex Minimate 0.25 m single grating spectrometer was used to obtain fast (~ 1 min) scans across a broad spectral range (3.5–1.8 eV). This allows us to measure the time dependence of the spectra. The focused laser spot has a diameter ~ 1.3 mm.

Figure 1 shows the time dependence of spectra from the Ar (440 V) sample under low power UV illumination. This sample has by far the brightest YL and is the only sample to show YL at room temperature. A very clear transition is visible from the BL at ~ 3.0 eV to the YL at ~ 2.2 eV as a function of time. Although the relative intensities of the BL and YL clearly depend on the spectral response of the optical components employed, we believe that Fig. 1 gives a reasonable qualitative representation of what is observed by the naked eye: the illuminated spot is initially bright blue and becomes bright yellow after less than 5 min. Due to long (~ 1 min) scan times in Fig. 1, quantitative data on the tran-

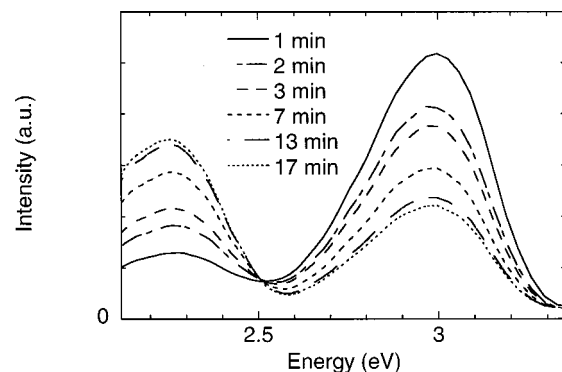


FIG. 1. Evolution from BL (~ 3.0 eV) to YL (~ 2.2 eV) at 24 K over 17 min with $P_{\text{laser}} = 1.4$ mW. The change is visible to the naked eye after less than 5 min. Band edge PL (UV band) is not shown.

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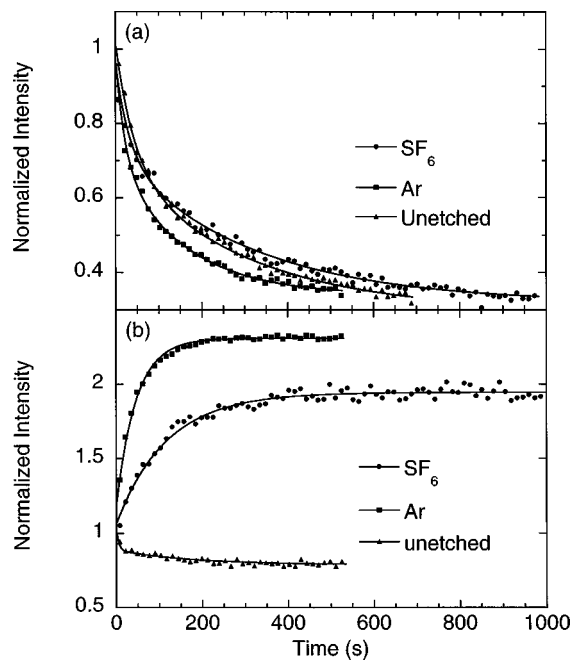


FIG. 2. Normalized time dependence of the BL (a) and YL (b) at 24 K with $P_{\text{laser}} = 5$ mW. For clarity, only every 10th data point is shown. Empirically it is found that the data can be fitted with either biexponential (for the BL) or exponential (for the YL) curves, enabling decay rates to be quantified.

sition from BL to YL is obtained from decay curves measured at fixed energy (Fig. 2). When kept at low temperatures the spot continues to emit yellow light (when reilluminated) for at least 12 h, the longest time tested to date. Similar behavior is observed in the Ar (78 V) sample. These properties indicate that the Ar-etched material has potential for optical memory applications.¹¹

Figure 2(a) compares BL decay curves for the Ar (440 V), SF_6 (440 V), and unetched samples. The behavior of all

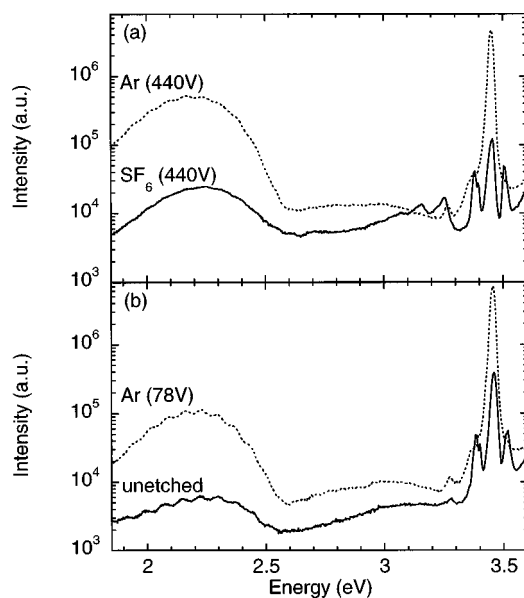


FIG. 3. PL over a wide spectral range from all four samples at 24 K after the transition from BL to YL has been completed. Note the log scale. The free and bound excitons are not resolved and contribute to the peak near 3.47 eV. The BL appears weaker than in Fig. 1 because the photomultiplier tube used here has a lower blue sensitivity. Weak peaks at 3.51 and 3.40 eV are due to scattered light from imperfectly filtered additional laser lines (many orders of magnitude weaker than the main line at 333.8 nm).

TABLE I. Comparison of UV PL, BL, and YL peak intensities for each sample after the transition from BL to YL has been completed.

	UV	BL	YL	UV/BL	UV/YL	YL/BL
Ar (440 V)	4.6×10^6	1.4×10^4	5.2×10^5	340	8.8	39
Ar (78 V)	7.0×10^6	1.0×10^4	1.1×10^5	700	64	11
SF_6 (440 V)	1.2×10^5	8.0×10^3	2.5×10^4	15	4.9	3.1
Unetched	3.9×10^5	4.7×10^3	6.2×10^3	82	62	1.3

three samples is comparable, although the decay is slightly faster for the Ar (440 V) sample. The decay curves in Fig. 2(a) have been normalized to enable comparison—note that the absolute intensities are very different (see later). The observed decay rates increase approximately linearly with increasing laser power (not shown). Figure 2(b) shows the normalized time dependences for the YL. The characteristic times for the two etched samples are again similar, but the Ar (440 V) sample changes more quickly and exhibits a larger relative change in intensity. The unetched sample shows clearly different time dependent behavior—the illumination intensity dependence for this sample is, however, complicated and is under further investigation.

The rapidly changing BL and YL bands ensure that meaningful comparison between samples can only be made at long times. Figure 3 compares broadband low-resolution spectra from all four samples after illumination for 20 min with 20 mW illumination to ensure that each sample is in the final state of the transition from the BL to the YL. The band edge PL is observed at around 3.47 eV in each sample (we will refer to this as the UV PL). The weaker peaks observed in the range 3.1–3.4 eV will be discussed elsewhere. There is an enormous variation in the strength of the UV PL between samples—the Ar-etched samples exhibit UV PL and YL which is much brighter than for the unetched and SF_6 etched samples. At long times the BL band is weak in all samples. The intensities of the UV PL, BL, and YL after a long period of illumination are summarized in Table I.

Figure 4 shows the band edge PL in more detail. As discussed previously¹⁰ the unetched sample shows the A_1 exciton at 3.477 eV, B_1 exciton at 3.483 eV, and negligible luminescence from bound excitons. The temperature dependence of the spectra from the etched samples allows us to identify the peaks at 3.471 and 3.460 eV with donor bound exciton (D^0X) and acceptor bound exciton (A^0X) peaks, respectively. Spectra from both Ar-etched samples are com-

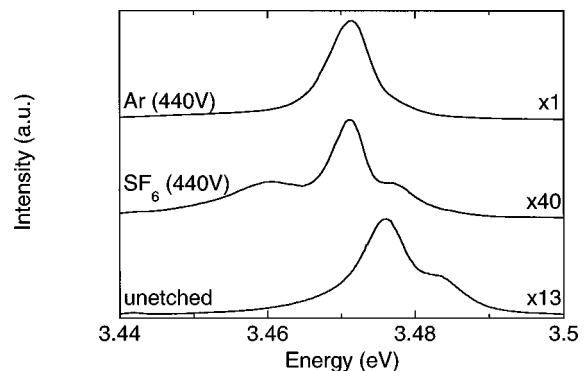


FIG. 4. Comparison of band edge PL spectra at 24 K with $P_{\text{laser}} = 5$ mW. Note the multiplier on the right-hand side.

pletely dominated by the D^0X peak indicating an enormous increase in the number of donors in these samples. Note, however, that the free excitons A_1 and B_1 have not been eliminated, they are *masked* by the D^0X peak at low temperatures. The UV PL is not observed to vary significantly with time.

Table I and Figs. 3 and 4 clearly show that the strength of the YL correlates to some extent with the strength of the D^0X peak—when compared with the unetched sample all etched samples show an absolute increase in the D^0X intensity *and* an increase in the YL. This suggests that the YL is in some way related to the presence of donors in the material. The picture is, however, complicated by the different intensity ratios UV/YL (see later). Note that the SF_6 -etched sample has the weakest UV PL *and* YL of the etched samples, indicating that fewer donors have been introduced. Possible explanations include a lower production rate of donors during etching due to the greater size of the SF_6 molecule or continual removal of surface material, including introduced donors, by the SF_6 plasma (it is an efficient etchant¹⁰ whereas the argon plasma is inert).

The metastable defects, BL to YL transition, and decay times induced here by RIE appear to have strong similarities to those observed recently in unetched GaN.¹² Although it has not been investigated in detail, a BL band has commonly been observed^{3,4,5,12–14} in conjunction with the YL. In addition, the weakness of the BL (after long or intense UV exposures—Fig. 3) makes it likely that BL can be observed in other samples with more careful measurements. Hence, we believe that any model of the YL must also be able to account for the existence of the BL and allow for the possibility of a transfer of intensity from BL to YL.

We now turn to a comparison of our data with proposed models of the YL. In the simple model proposed in Refs. 2 and 3 the intensity ratio $UV/YL \propto N_D/N_T$ where N_D is the donor concentration and N_T the concentration of deep traps. This model suggests that the similar UV/YL ratio but very different UV and YL intensities (Table I) for the unetched and Ar (78 V) samples can be explained by a simple compensation effect ($N_T \propto N_D$), consistent with the results of Ref. 3. The much smaller UV/YL ratios for the SF_6 (440 V) and Ar (440 V) samples are not, however, consistent with $N_T \propto N_D$. In this model^{2,3} the reduced UV/YL ratio suggests an increased density of deep traps, with $N_T \propto N_D^i$ and $i > 1$. This might be consistent with the proposal that $N_T \propto N_D^3$ for Ga vacancies.^{3,7} For large ion energies (440 V) it would appear that the compensating center (deep trap) is more strongly activated (or that there are stronger nonradiative processes affecting free carriers) than in the unetched and Ar (78 V) samples. Note, however, that neither this model,^{2,3} nor many of the others that we are aware of,^{4–8} are able to explain either the BL or the metastable nature of the defect.

Glaser *et al.*⁹ found evidence for a deep donor state and their model (Fig. 10 in Ref. 9) of a metastable donor/deep donor state could account for both the BL and YL if the acceptor were a deep (~ 0.9 eV—as in Ref. 4) rather than a shallow (~ 0.19 eV) acceptor state. However, since the D^0X peak intensity does not change significantly with time, we suggest that the donors themselves are *not* metastable and so play an *indirect* role in the YL.

We note finally that: (1) The characteristic times observed here (Fig. 2) are comparable to the rise time for the persistent photoconductivity (PPC) effect observed in GaN. Since the mechanisms of PPC¹⁵ and the optical memory effects observed in GaN¹¹ must involve metastable deep defects, it seems likely that the same mechanism is responsible for the transition from BL to YL observed here and in Ref. 12. (2) It is interesting to speculate on the relationship between our results and the observed transition from YL to BL with increasing hydrostatic pressure.¹⁴ A model of metastable defects which includes lattice relaxation¹⁶ might also explain a change in defect state with increasing pressure.

In conclusion, metastable defects have been introduced into GaN by RIE. The defects contribute to both the blue and yellow PL bands and the data provide a stern test for theories of the ubiquitous YL. Further theoretical developments must include a detailed model of compensating centers and lattice relaxation.

¹S. Nakamura and G. Fasol, *The Blue Laser Diode: GaN Based Light Emitters and Lasers* (Springer, New York, 1997).

²W. Grieshaber, E. F. Schubert, I. D. Goepfert, R. F. Karlicek, Jr., M. J. Schurman, and C. Tran, *J. Appl. Phys.* **80**, 4615 (1996).

³E. F. Schubert, I. D. Goepfert, and J. M. Redwing, *Appl. Phys. Lett.* **71**, 3224 (1997).

⁴T. Ogino and M. Aoki, *Jpn. J. Appl. Phys., Part 1* **19**, 2395 (1980).

⁵D. M. Hofmann, D. Kovalev, G. Steude, B. K. Meyer, A. Hoffmann, L. Eckey, R. Heitz, T. Detchprom, H. Amano, and I. Akasaki, *Phys. Rev. B* **52**, 16702 (1995); A. Hoffmann, L. Eckey, P. Maxim, J.-Chr. Holst, R. Heitz, D. M. Hoffman, D. Kovalev, G. Stevde, D. Volm, B. K. Meyer, T. Detchprom, K. Hiramatsu, H. Amano, and I. Akasaki, *Solid-State Electron.* **41**, 275 (1997).

⁶H. M. Chen, Y. F. Chen, M. C. Lee, and M. S. Feng, *Phys. Rev. B* **56**, 6942 (1997).

⁷J. Neugebauer and C. Van de Walle, *Appl. Phys. Lett.* **69**, 503 (1996).

⁸T. Suski, P. Perlin, H. Teisseyre, M. Leszczynski, I. Grzegory, J. Jun, M. Boćkowski, S. Porowski, and T. D. Moustakas, *Appl. Phys. Lett.* **67**, 2188 (1995).

⁹E. R. Glaser, T. A. Kennedy, K. Doverspike, L. B. Rowland, D. K. Gaskill, J. A. Freitas, Jr., M. A. Khan, D. T. Olson, J. N. Kuznia, and D. K. Wickenden, *Phys. Rev. B* **51**, 13326 (1995).

¹⁰R. Cheung, S. Withanage, R. J. Reeves, S. A. Brown, I. Ben-Yaacov, C. Kirchner, and M. Kamp, *Appl. Phys. Lett.* **74**, 3185 (1999).

¹¹V. A. Joshkin, J. C. Roberts, F. G. McIntosh, S. M. Bedair, E. L. Piner, and M. K. Behbehani, *Appl. Phys. Lett.* **71**, 234 (1997); I. K. Shmagin, J. F. Muth, R. M. Kolbas, R. D. Dupuis, P. A. Grudowski, C. J. Eiting, J. Park, B. S. Shelton, and D. J. H. Lambert, *ibid.* **71**, 1382 (1997); I. K. Shmagin, J. F. Muth, R. M. Kolbas, M. P. Mack, A. C. Abare, S. Keller, L. A. Coldren, U. K. Mishra, and S. P. DenBaars, *ibid.* **71**, 1455 (1997).

¹²S. J. Xu, G. Li, S. Chua, X. Wang, and W. Wang, *Appl. Phys. Lett.* **72**, 2451 (1998).

¹³W. Shan, T. J. Schmidt, R. J. Hauenstein, J. J. Song, and B. Goldenberg, *Appl. Phys. Lett.* **66**, 3492 (1995).

¹⁴P. Perlin, T. Suski, H. Teisseyre, M. Leszczynski, I. Grzegory, J. Jun, S. Porowski, P. Boguslawski, J. Bernholc, J. C. Chervin, A. Polian, and T. D. Moustakas, *Phys. Rev. Lett.* **75**, 296 (1995).

¹⁵H. M. Chen, Y. F. Chen, M. C. Lee, and M. S. Feng, *Appl. Phys. Lett.* **82**, 899 (1997); C. H. Qiu, W. Melton, M. W. Leksono, J. I. Pankove, B. P. Keller, and S. P. DenBaars, *ibid.* **69**, 1282 (1996); F. Binet, J. Y. Duboz, N. Laurent, C. Bonnat, P. Collot, F. Hanauer, O. Briot, and R. L. Aulombard, *ibid.* **72**, 960 (1998); C. H. Qiu and J. I. Pankove, *ibid.* **70**, 1983 (1997); G. Beadie, W. S. Rabinovich, A. E. Wickenden, D. D. Koleske, S. C. Binari, and J. A. Freitas, Jr., *ibid.* **71**, 1092 (1997); C. Johnson, J. Y. Lin, H. X. Jiang, M. Asif Khan, and C. J. Sun, *ibid.* **68**, 1808 (1996); J. Z. Li, Y. Lin, H. X. Jiang, A. Salvador, A. Botchkarev, and H. Morkoc, *ibid.* **69**, 1474 (1996).

¹⁶T. Mattila, A. Seitsonen, and R. Nieminen, *Phys. Rev. B* **54**, 1474 (1996); J. Neugebauer and C. Van de Walle, *ibid.* **50**, 8067 (1994).