

Spectroscopy of competing mechanisms generating stimulated emission in gallium nitride

W. D. Herzog,^{a)} G. E. Bunea, M. S. Ünlü, and B. B. Goldberg

Department of Electrical and Computer Engineering, Department of Physics, and Center for Photonics Research, Boston University, Boston, Massachusetts 02215

R. J. Molnar

Massachusetts Institute of Technology, Lincoln Laboratory, Lexington, Massachusetts 02420

(Received 10 April 2000; accepted for publication 16 October 2000)

Two competing recombination mechanisms of stimulated emission in the vicinity of 145 K have been directly observed in the temperature dependence of the optical emission spectra for high-quality, unintentionally doped gallium nitride. Our analysis of the spectra indicates that exciton-exciton scattering is responsible for stimulated emission below 145 K, while at higher temperatures an electron-hole plasma becomes the dominant mechanism. © 2000 American Institute of Physics. [S0003-6951(00)02051-9]

Gallium nitride and its alloys constitute an important class of materials for the development of UV/blue/green optoelectronic devices and high power, high temperature electronics.¹ Over the past few years the successful commercialization of these technologies has been achieved with materials produced by metalorganic chemical vapor deposition (MOCVD) and to a lesser extent by molecular beam epitaxy (MBE). Recently, tremendous progress has been achieved in growing high quality films by hydride vapor phase epitaxy (HVPE).²⁻⁴ MOCVD and MBE have lower growth rates, providing for the control necessary to produce thin films for quantum wells and precise heterostructures. However, HVPE can produce thick films which are useful for homojunction devices and may also serve as substrates for epitaxial growth by other techniques. Ultimately, the successful development of GaN grown by HVPE will result in the reduction of production costs. In this letter we present results on the optical properties of GaN for high excitation densities. Based on the optical and transport properties of the HVPE-grown sample we studied,⁵ we believe that our results are representative of high quality, undoped GaN material irrespective of the growth method.

For high excitation densities and/or temperatures, the recombination mechanisms in GaN have not yet been well established. Excitons have been observed in absorption measurements at room temperature.⁶ However, charge screening of the Coulomb interaction under conditions of high carrier density is likely to lead to thermal ionization of the exciton. In order to ascertain the stability of excitons at elevated carrier densities, we have performed temperature dependent spectroscopy of the optical recombination mechanisms under conditions of strong optical pumping.

At low temperatures and for low power densities of optical pumping the photoluminescence is dominated by the recombination of excitons. As the level of optical pumping is increased, previous measurements have suggested a number of mechanisms responsible for gain in GaN. While it has

been reported that an electron-hole plasma is responsible for low temperature gain,⁷ it is more likely a result of exciton-exciton scattering.⁸⁻¹² These measurements and others also indicate that as the temperature is increased above ~ 150 K, the relative increase in the population of free carriers to excitons resulted in charge screening of the Coulomb interaction of the exciton recombination.⁸⁻¹³ Our results provide direct spectral evidence of this crossover of optical recombination mechanisms. We observe competition in the optical recombination between exciton-exciton scattering and an electron-hole plasma in the spectra of the stimulated emission.

Our experiments were carried out on a $63 \mu\text{m}$ thick film of GaN grown on a (0001) sapphire substrate. The material was grown by a chloride-transport HVPE vertical reactor at a growth rate of $21 \mu\text{m/h}$. Hall measurements indicate the sample is unintentionally doped *n* type with a carrier concentration of $6 \times 10^{16} \text{cm}^{-3}$. Details of the growth and observation of stimulated emission have been previously reported.² Temperature dependent time-resolved photoluminescence (PL) studies have also been reported for this sample.⁵ The radiative recombination lifetime was found to be 295 and 530 ps for the free and donor-bound excitons at 4 K. The room temperature radiative recombination lifetime was found to be 530 ps. Both low temperature and room temperature time-resolved data displayed a single exponential decay indicating the absence of strong nonradiative recombination.

Figure 1 shows the temperature dependence of the time-integrated PL spectra. At 4 K the spectra is dominated by the donor-bound exciton peak at ~ 3.47 eV with the free exciton recombination appearing as a shoulder on the high energy side of the PL peak. The PL peak at ~ 3.45 eV has been attributed to an acceptor-bound exciton^{14,15} and the ~ 3.378 eV peak has been attributed to either a longitudinal optical (LO) phonon replica of the exciton¹⁶ or a free to bound transition of a 116 meV impurity.^{14,15} At elevated temperatures the 3.378 eV PL peak can be seen to merge into the tail of the exciton PL. Finally, the 2LO phonon replica of the exciton can also be discerned at ~ 3.3 eV in the 4 K spectrum.

In order to study stimulated emission, the sample was

^{a)}Electronic mail: wherzog@ll.mit.edu

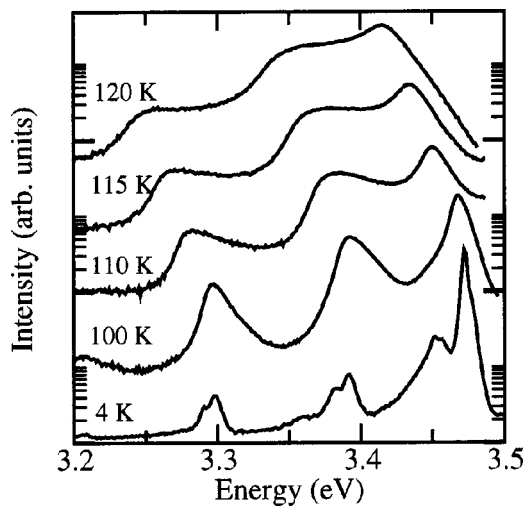


FIG. 1. Temperature dependence of time-integrated photoluminescence from 4 K (bottom spectrum) to 120 K (top spectrum). Photoluminescence intensity is shown on a logarithmic scale. Spectra are offset for clarity.

excited using a nitrogen laser with a ~ 4 ns pulse width and a peak energy of $200 \mu\text{J}$ per pulse. Stimulated emission measurements were carried out on a small ($\sim 1 \text{ mm}^2$) piece of the sample that was broken from the wafer. The sample was mounted on the cold finger of a continuous-flow cryostat. Liquid nitrogen was used in conjunction with a heater and control electronics to carry out temperature dependent measurements from 100 K to room temperature. The optical emission was collected from the edge of the sample and focused onto the slits of a 0.64 m spectrometer and dispersed onto a charge-coupled device (CCD) camera. The spectral resolution of our system was 0.2 nm.

Figure 2 shows PL spectra obtained at 115 and 175 K. Plotted for each temperature is a spectrum collected for pump intensities below and above the power density necessary to achieve stimulated emission. For optical pumping intensities just below the threshold for stimulated emission we can see the exciton PL peak followed by the LO phonon replicas for both temperatures shown. For pump powers above threshold, the 115 K spectrum shows the stimulated emission at 3.413 eV, 37.3 meV below the peak of the spontaneous emission. At 170 K we see a similar spectrum, al-

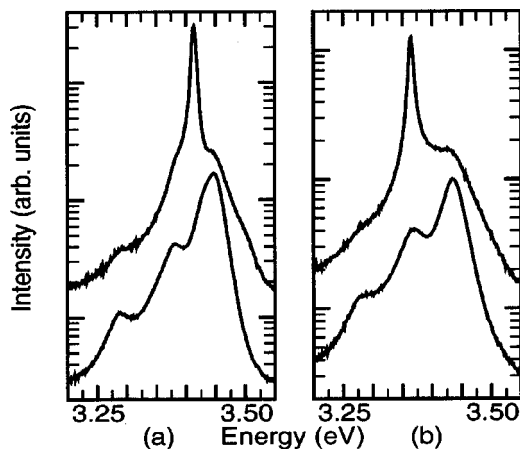


FIG. 2. Spontaneous and stimulated emission spectra generated at excitation power densities of 3 and 0.1 MW/cm^2 for temperatures of 115 K (a) and 170 K (b). Intensity is plotted on a logarithmic scale.

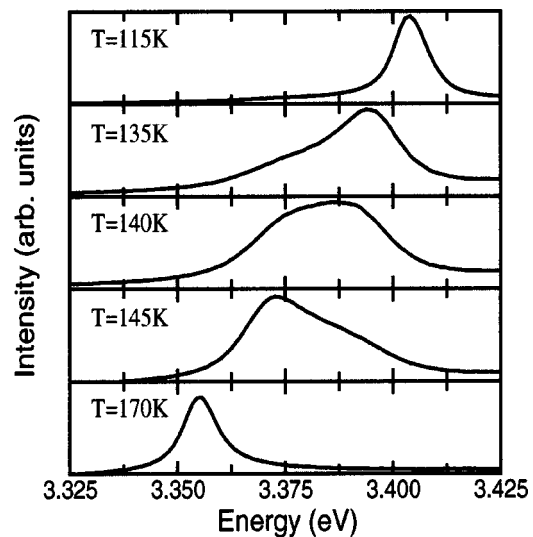


FIG. 3. Stimulated emission spectra for temperatures ranging from 115 to 170 K for an excitation power density of 3 MW/cm^2 . Intensity is shown on a linear scale.

though the stimulated emission is redshifted from the exciton by 65.3 meV and overlaps the peak attributed to the phonon replica for this specific temperature. The temperature dependence between 115 and 170 K is the region in which the energy spacing between the stimulated and spontaneous emission begins to diverge. Below we detail the spectral measurements in this temperature range.

Two competing mechanisms contributing to the stimulated emission can clearly be seen in the temperature dependent spectra shown in Fig. 3. Spectra were collected for a pump power of ~ 1.6 times the threshold of stimulated emission. At 115 K we observe the stimulated emission peak at 3.413 eV with a full width at half-maximum (FWHM) of 9 meV. At higher temperatures a shoulder becomes evident on the low energy side of the stimulated emission peak as can be seen in the 135 K spectrum. The low energy shoulder becomes equal in intensity to the higher energy stimulated emission peak at a temperature of 140 K, yielding a FWHM that is much broader due to the existence of two competing recombination mechanisms. For temperatures well above the crossover the stimulated emission is completely dominated by the lower energy recombination mechanism and the emission linewidth is comparable to the linewidth observed for the low temperature stimulated emission. This can be seen in the spectrum taken at 170 K.

Now we turn our attention to identifying the two distinct recombination mechanisms of stimulated emission in the vicinity of 145 K. Figure 4 summarizes the temperature dependence of the stimulated (open circles) and spontaneous (filled circles) emission peak energies. For temperatures below 145 K we observe an energy separation between the peaks for the exciton PL and the stimulated emission which is significantly greater than the exciton binding energy. For an exciton-exciton scattering mechanism, the emission energy should be lower than the exciton photoluminescence by the binding energy of the exciton, plus the kinetic energy of the free electron-hole pair created during the collision.¹⁷ Consequently, we attribute the stimulated emission in the lower temperature range to exciton-exciton scattering.

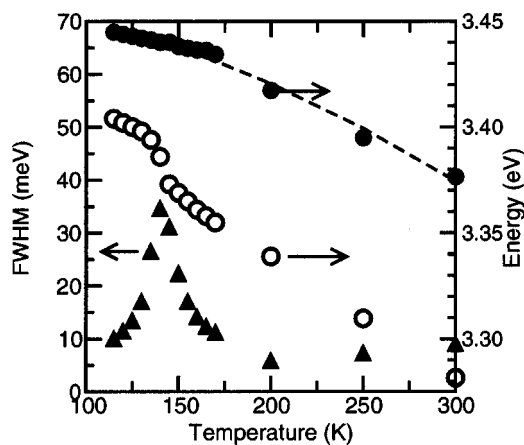


FIG. 4. Spontaneous emission peak position (filled circles), stimulated emission peak position (open circles), and stimulated emission FWHM (triangles) vs temperature. Varshni's dependence of the band gap with temperature is given by the dashed line to serve as a guide to the eye.

As the temperature increases above 145 K the population of free carriers screen the Coulomb interaction of the exciton. The free carriers are generated by the partial thermal ionization of the exciton population and also by the inelastic exciton-exciton collisions. As a result, an electron hole plasma becomes the dominant mechanism for stimulated emission.

In the vicinity of the crossover of stimulated emission mechanisms at 145 K, we observe a sudden shift in the stimulated emission peak position to lower energies. The energy separation between the spontaneous and stimulated emission peaks continues to redshift as the temperature is increased. At room temperature, the energy separation between the spontaneous emission and the stimulated emission is 95 meV.

Further confirmation of our interpretation is provided by stimulated emission results from two intentionally doped GaN samples grown by the HVPE method. Heavily doped samples should exhibit stimulated emission from exciton-exciton scattering only at much lower temperatures than is observed for the undoped material due to additional charge screening. Our stimulated emission results from samples with carrier concentrations of 2×10^{18} and $8 \times 10^{18} \text{ cm}^{-3}$ do not exhibit a crossover in the mechanism of stimulated emission for temperatures as low as 77 K. Furthermore, the energy separation between the stimulated emission and spontaneous emission for these two samples is greater than that observed from the unintentionally doped sample at its crossover to recombination via an electron-hole plasma. This

leads us to believe that stimulated emission from intentionally doped material is due to an electron-hole plasma for temperatures between 77 K and room temperature.

In conclusion we present direct spectral evidence for competition between two stimulated emission mechanisms in GaN. Our temperature dependent optical emission spectra clearly demonstrate peaks from two separate recombination processes. We also observe a dramatic change in the FWHM of the stimulated emission in the vicinity of the crossover temperature due to the coexistence of two recombination mechanisms. The stimulated emission for temperatures below 150 K is consistent with exciton-exciton scattering. For temperatures greater than 150 K stimulated emission is due to recombination of an electron-hole plasma.

This research is partially supported by NSF CAREER Grant No. ECS 9625236, NSF ARI Grant No. 9413855 and by ARO Grant No. DAAG-55-98-1-0143. The work at Lincoln Laboratory was sponsored by the Defense Advanced Research Projects Agency under Air Force Contract No. F19628-95-C-0002.

- ¹S. Strite and H. Morkoç, *J. Vac. Sci. Technol. B* **10**, 1237 (1992).
- ²R. J. Molnar, W. Götz, L. T. Romano, and N. M. Johnson, *J. Cryst. Growth* **178**, 147 (1997).
- ³M. K. Kelly, R. P. Vaudo, V. M. Phanse, L. Gorgens, O. Ambacher, and M. Stutzman, *Jpn. J. Appl. Phys., Part 2* **38**, L217 (1999).
- ⁴A. Usui, H. Sunakawa, A. Sakia, and A. A. Yamaguchi, *Jpn. J. Appl. Phys., Part 2* **36**, L899 (1997).
- ⁵G. E. Bunea, W. D. Herzog, M. S. Ünlü, B. B. Goldberg, and R. J. Molnar, *Appl. Phys. Lett.* **75**, 838 (1999).
- ⁶A. J. Fischer, W. Shan, J. J. Song, Y. C. Chang, R. Horning, and B. Goldenberg, *Appl. Phys. Lett.* **71**, 1981 (1997).
- ⁷S. Hess, R. A. Taylor, J. F. Ryan, B. Beaumont, and P. Gibart, *Appl. Phys. Lett.* **73**, 199 (1998).
- ⁸J.-Chr. Holst, L. Eeckey, A. Hoffman, I. Broser, H. Amano, and I. Akasaki, *MRS Internet J. Nitride Semicond. Res.* **2**, 25 (1997).
- ⁹L. Eeckey, J.-Chr. Holst, A. Hoffman, I. Broser, T. Detchprohm, and K. Hiramatsu, *MRS Internet J. Nitride Semicond. Res. IJNF7* **2**, 1 (1997).
- ¹⁰S. Bidnyk, T. J. Schmidt, B. D. Little, and J. J. Song, *Appl. Phys. Lett.* **74**, 1 (1999).
- ¹¹L. Eeckey, J. Holst, V. Kutzer, A. Hoffman, I. Broser, O. Ambacher, M. Stutzmann, H. Amano, and I. Akasaki, *Mater. Res. Soc. Symp. Proc.* **468**, 237 (1997).
- ¹²S. Bidnyk, J. B. Lam, B. D. Little, Y. H. Kwon, J. J. Song, G. E. Bulman, H. S. Kong, and T. J. Schmidt, *Appl. Phys. Lett.* **75**, 3905 (1999).
- ¹³S. Bidnyk, B. D. Little, T. J. Schmidt, Y. H. Cho, J. Krasinski, J. J. Song, B. Goldenberg, W. Yang, W. G. Perry, M. D. Bremser, and R. F. Davis, *J. Appl. Phys.* **85**, 1792 (1999).
- ¹⁴O. Lagerstedt and B. Monemar, *J. Appl. Phys.* **45**, 2266 (1974).
- ¹⁵M. Ilegems, R. Dingle, and R. A. Logan, *J. Appl. Phys.* **43**, 3797 (1972).
- ¹⁶A. K. Viswanath, J. I. Lee, S. Yu, D. Kim, Y. Choi, and C. Hong, *J. Appl. Phys.* **84**, 3848 (1998), and references therein.
- ¹⁷I. Galbraith and S. W. Koch, *J. Cryst. Growth* **159**, 667 (1996).