Time-resolved photoluminescence investigations of cubic GaN layers and crystals up to room temperature

R. Klann,[a] O. Brandt, H. Yang,[b] H. T. Grahn,[c] and K. H. Ploog

Paul-Drude-Institut für Festkörperelektronik, D-10117 Berlin, Germany

We compare the recombination dynamics of GaN single crystals to that of epitaxial cubic GaN layers on GaAs(001) using picosecond photoluminescence (PL) spectroscopy. At low temperatures, the band-edge PL decay time of the layer is much shorter than that of the crystals, evidencing the importance of nonradiative processes in the case of the layer. However, at room temperature both the emission spectra and their decay times of layer and crystals are almost identical. At 300 K the decay times are short (10 ps) for low excitation density and increase to values of 100 ps at moderate excitation density reflecting the saturation of nonradiative recombination channels. © *1997 American Institute of Physics.* [S0003-6951(97)03814-X]

Cubic GaN crystals with high structural and optical quality have been realized using molecular beam epitaxy (MBE).[1–3] These crystals are virtually free of structural defects and appear to be chemically pure as their cathodoluminescence spectra are dominated by exciton transitions at any temperature.[2] In comparison, epitaxial cubic layers grown on GaAs(001) contain a high density of structural defects,[4] and their low-temperature photoluminescence (PL) spectra are dominated by donor-acceptor transitions. Time-resolved PL spectroscopy has been employed to investigate the recombination processes both in hexagonal[5–9] and cubic[10] GaN. In any case, it was concluded that nonradiative recombination plays an important role even at low temperature.

In this letter we compare the transient PL spectra and the decay times of cubic GaN layers with a thickness of about 1 μm with that of GaN single crystals of μm size. This comparison of GaN samples with drastically different impurity and defect concentrations allows for an interesting insight into the role of these impurities and defects for the optical properties of GaN. In fact, at low temperatures the decay time of the band edge transition of the cubic GaN layer is much shorter than that of the crystals. Moreover, impurity-related transitions are present in the time-resolved spectra of the layer. However, at room temperature the spectra of the layer and the crystals coincide and the PL decay times are identical. At 300 K the PL intensity as well as the decay time increase with increasing excitation density, demonstrating the saturation of nonradiative recombination centers.

The samples under investigation are grown by solid-source MBE employing a dc plasma discharge source for dissociating molecular N_2 into activated nitrogen species. GaAs(001) is used as the substrate material. The GaN layer (sample L) is grown at stoichiometric conditions as revealed by the (2×2)-reconstructed surface during growth.[11] The rms surface roughness of sample L as measured by atomic force microscopy (AFM) is 10 nm. X-ray diffraction shows this sample to be predominantly cubic since no wurtzite re-

flections are detected.[12] In order to achieve crystals of high structural perfection with a typical diameter of about 3 μm (sample C), the Ga flux is increased by a factor of 4 after the deposition of a cubic template at stoichimetric conditions. Scanning electron microscopy reveals that a fraction ($\simeq 10\%$) of the crystals are hexagonal.[2] Transmission electron microscopy taken from both cubic and hexagonal crystals shows that the crystals are essentially free of structural defects such as stacking faults and dislocations.[1] Further details of the growth can be found in Ref. 12.

Time-resolved PL measurements are performed using a streak-camera system in synchro-scan operation in conjunction with a pulsed femtosecond Ti:sapphire laser (coherent mira). The 150 fs laser pulses with repetition rates of 76 MHz are frequency-doubled and -tripled resulting in excitation energies of 3.1–3.4 eV and 4.65–5.1 eV, respectively. The excitation power was reduced by neutral density filters and controlled by a power meter. If not stated otherwise, the excitation power is reduced to 60 μW. The typical diameter of the laser spot on the sample is $\sim$100 μm. The luminescence is dispersed by a 22 cm monochromator with a 600 lines/mm grating and focused onto the photocathode of the streak tube. The streak images are recorded by a cooled charge coupled devices (CCD) array. The spectral resolution amounts to 0.4 nm (3 meV) and the temporal resolution to 2 ps. The samples are mounted on the cold-finger of a He flow cryostat allowing continuous temperature control between 4.2 and 300 K.

Transient spectra for sample C recorded at 5 K are shown in Fig. 1 for an excitation energy of 4.85 (dashed line) and 3.36 eV (full line). Note that, for a photon energy of 3.36 eV, no carriers are excited in the hexagonal phase. Under both excitation conditions, the PL spectrum is dominated by a sharp line at 3.27 eV with a full width at half maximum (FWHM) of 10 meV and exhibits in addition a weaker line at 3.47 eV with a similar FWHM. It has been shown that these PL lines at 3.27 and 3.47 eV originate from exciton recombination in cubic and hexagonal crystals, respectively.[1,2,13]

The transient PL spectrum of sample L upon excitation at 4.85 eV is shown in Fig. 2 (full line). The FWHM of the PL line at 3.27 eV is broadened to 23 meV, and its intensity is reduced compared to sample C. An additional line in this spectral region is observed at 3.20 eV, which is not present

---

[a] Present address: CompuNet GmbH, Hörselbergstr. 7, D-81677 München, Germany.

[b] Present address: National Research Center for Optoelectronic Technology (NCOT), Institute of Semiconductors, Chinese Academy of Science, Beijing 100083, People's Republic of China.
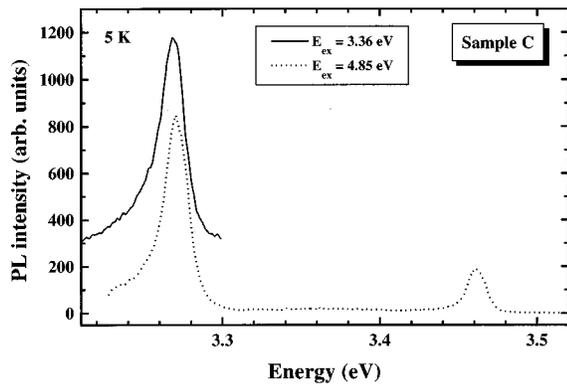
[c] Electronic mail: htg@pdi.wias-berlin.de

FIG. 1. Time-resolved PL spectra at 5 K averaged over the first 100 ps after excitation in sample C excited at 3.36 and 4.85 eV as indicated. The spectra have been shifted vertically.

in the time-resolved PL spectra of sample C (cf. Ref. 2). Also in the vicinity of the energy gap of the hexagonal phase two peaks are observed. The weaker one at 3.47 eV is at exactly at the same energy as the high energy peak in sample C (cf. Fig. 1). The intensity ratio of the hexagonal peak at 3.47 eV to the cubic peak at 3.27 eV is about ten times smaller in sample L than in sample C (note the scaling factor in Fig. 2).

The peaks at 3.20 and 3.42 eV in sample L are presumably caused by impurity-related transitions. While the two PL lines of sample C in Fig. 1 decay on a time scale of the order of 100 ps,[14] the defect-related PL signals at 3.42 and 3.20 eV decay on a nanosecond time scale. This can be seen in Fig. 2, where, in addition to the PL spectrum at short times, the spectrum 1 ns after photoexcitation (dashed line) is shown. The band edge peaks have almost disappeared on this time scale, while the two defect-related peaks dominate the spectrum. The identification of these two transitions as impurity-related transitions follows from this time dependent behavior.

The PL intensity transients at 5 K are plotted in Fig. 3(a) for sample C and in Fig. 3(b) for sample L. The temporal evolution of all lines contains an extremely fast rise time with a value within our time resolution. The PL decay at 3.27 eV for sample C is characterized by a bi-exponential time dependence. A fast relaxation (40 ps) dominates at short times, while a slower contribution (150 ps) follows at longer times. The emission at 3.27 eV remains unchanged in spec-
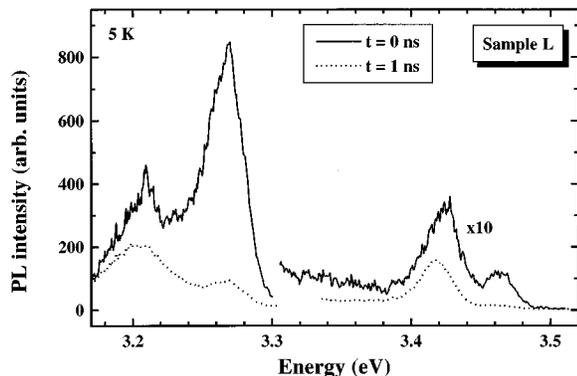

FIG. 2. Time-resolved PL spectra at 5 K in sample L excited at 4.85 eV averaged over 100 ps directly after excitation (full line) and after 1 ns (dotted line).
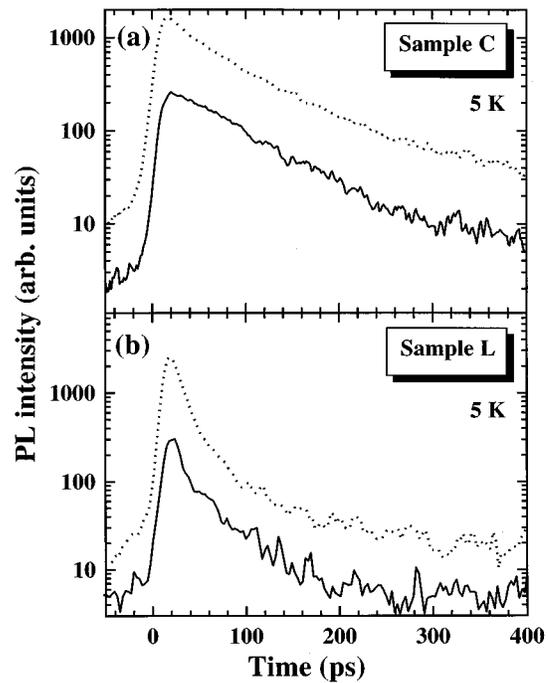

FIG. 3. PL transients of sample C (a) and sample L (b) at 5 K excited at 4.85 eV detected at 3.27 (dotted line) and 3.47 eV (solid line).

tral position, intensity, and time dependence for both excitation energies (cf. Ref. 13). The PL decay at 3.47 eV for sample C is characterized by a fast decay with a single time constant of 80 ps. However, the PL decay of both band edge peaks in sample L [Fig. 3(b)] exhibits a bi-exponential dependence with time constants of 15 and 50 ps, which are similar for the cubic and hexagonal peaks. The much faster initial decay in sample L suggests a substantial contribution of nonradiative processes. Since the impurity-related peaks at 3.2 and 3.4 eV exhibit a delayed onset compared to the respective band-edge transitions, we conclude that these processes are related to carrier capture by impurities.

The emission properties of sample L at 300 K are shown in Fig. 4. The inset depicts the PL spectrum for an excitation power of 2.25 mW. The PL peaks at 3.20 eV with a FWHM of 90 meV. The transients detected at 3.20 eV are shown in Fig. 4 for two different excitation powers of 0.20 (dashed line) and 2.25 mW (full line). For 0.20 mW, the rise time is again below our time resolution. The apparently slower rise time of the PL transient excited with 2.25 mW is only caused by the longer time window used for this measurement. For the lower excitation power the decay is single exponential with a decay time of 10 ps. However, increasing the excitation power by one order of magnitude results in an enhancement of the PL decay time to 70 ps. In addition, the integrated PL intensity rises superlinearly with the excitation density in this excitation regime indicating participation of bimolecular recombination between free carriers.[14] These observations suggest a saturation of nonradiative recombination channels. The observed recombination lifetimes in sample L are identical to those for sample C and for high excitation are comparable to lifetimes observed in high-quality hexagonal GaN layers on sapphire.[6]

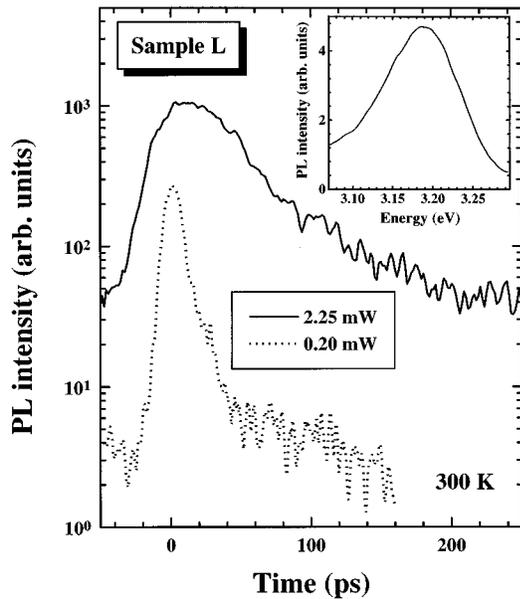In conclusion, we have studied the dynamics of the near-

FIG. 4. Room temperature PL transients of sample L excited at 3.36 eV for an excitation power of 0.2 (dotted line) and 2.25 mW (full line) and a detection energy of 3.20 eV. The inset depicts the transient PL spectrum averaged over the first 100 ps using an excitation power of 2.25 mW.

band-edge emission for GaN single crystals and epitaxial GaN layers containing a high density of structural defects. At 5 K, the GaN layer exhibits a much faster initial decay compared to the GaN crystals, indicating the presence of additional nonradiative processes which are presumably related to carrier capture by impurities. In contrast, the room temperature spectra are almost identical for both samples with a PL decay time of 10 ps at low excitation power. With increasing excitation power, the PL decay time increases, which is accompanied by a superlinear increase of the PL intensity. Thus, the nonradiative channels present in both samples are readily saturated. The striking similarity of the room temperature recombination dynamics for samples of drastically different structural perfection suggests that the structural defects present in the GaN layer (predominantly edge dislocations and stacking faults) do not act as nonradiative centers, but are electronically inert.

[1] R. Klann, H. Yang, O. Brandt, H. T. Grahn, and K. H. Ploog, Phys. Rev. B **52**, R11615 (1995).
[2] J. Menniger, U. Jahn, H. Yang, O. Brandt, and K. H. Ploog, Phys. Rev. B **53**, 1881 (1996).
[3] J. Müllhäuser, O. Brandt, H. Yang, and K. H. Ploog, in: *Gallium Nitride and Related Compounds*, edited by F. A. Ponce, R. D. Dupuis, S. Nakamura, and J. A. Edmond, Mater. Res. Soc. Symp. Proc. (Materials Research Society, Pittsburgh, 1996), Vol. 395, p. 607.
[4] O. Brandt, H. Yang, J. R. Müllhäuser, A. Trampert, and K. H. Ploog, Mater. Sci. Eng. B **43**, 215 (1997).
[5] M. Smith, G. D. Chen, J. Z. Li, H. X. Jiang, A. Salvador, W. K. Kim, O. Aktas, A. Botchkarev, and H. Morkoç, Appl. Phys. Lett. **67**, 3387 (1995).
[6] A. Hangleiter, J. S. Im, T. Forner, V. Härle, and F. Scholz, in Ref. 3, p. 559.
[7] B. Monemar, J. P. Bergman, H. Amano, I. Akasaki, T. Detchprohm, K. Hiramatsu, and N. Sawaki, *Proceedings of the International Symposium on Blue Laser and Light Emitting Diodes*, edited by A. Yoshikawa, K. Kishino, M. Kobayashi, and T. Yasuda (Ohmsha, Tokyo, 1996), p. 135.
[8] M. Goldlewski, A. Wysmolek, K. Pakula, J. M. Baranowski, I. Grzegory, J. Jun, S. Porowski, J. P. Bergman, and B. Monemar, in Ref. 7, p. 356.
[9] Y. Kawakami, Z. G. Peng, Y. Narukawa, S. Fujita, and S. Nakamura, Appl. Phys. Lett. **69**, 1414 (1996).
[10] H. Okumura, K. Ohta, W. W. Rühle, T. Nagatomo, and S. Yoshida, Inst. Phys. Conf. Ser. No. 142 (IOP, Bristol, 1996), p. 939.
[11] H. Yang, O. Brandt, and K. Ploog, J. Electron. Mater. **25**, 787 (1996).
[12] H. Yang, O. Brandt, and K. Ploog, Phys. Status Solidi **194**, 109 (1996).
[13] R. Klann, O. Brandt, H. Yang, H. T. Grahn, and K. H. Ploog, in Ref. 7, p. 198.
[14] R. Klann, O. Brandt, H. Yang, H. T. Grahn, and K. H. Ploog, Appl. Phys. Lett. **70**, 1076 (1997).