AIP | Applied Physics Letters

Dynamics of a bandedge transition in GaN grown by molecular beam epitaxy

M. Smith, G. D. Chen, J. Y. Lin, H. X. Jiang, A. Salvador, B. N. Sverdlov, A. Botchkarev, and H. Morkoç

Citation: Applied Physics Letters **66**, 3474 (1995); doi: 10.1063/1.113768
View online: http://dx.doi.org/10.1063/1.113768
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/66/25?ver=pdfcov
Published by the AIP Publishing

Dynamics of a band-edge transition in GaN grown by molecular beam epitaxy

M. Smith, G. D. Chen,[a] J. Y. Lin, and H. X. Jiang
Department of Physics, Kansas State University, Manhattan, Kansas 66502-2601

A. Salvador, B. N. Sverdlov, A. Botchkarev, and H. Morkoç
Materials Research Laboratory and Coordinated Science Laboratory, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

(Received 15 February 1995; accepted for publication 26 April 1995)

Time-resolved photoluminescence spectroscopy has been used to probe the dynamics of optical transitions in GaN epitaxial layers grown by molecular beam epitaxy. In particular, systematic measurements on a band-edge transition at about 3.42 eV have been carried out. Recombination lifetimes of this transition have been measured at different emission energies. Our results clearly show that the time-resolved photoluminescence can provide immense value in the understanding of the dynamic processes of optical transitions in GaN. © *1995 American Institute of Physics.*

GaN and $Al_xGa_{1-x}N$ wide band-gap semiconductors have been intensively studied[1–5] recently for applications in two areas: (1) optical devices, including blue-UV light emitting diodes (LED) and blue-UV laser diodes: (2) electronic devices, including devices operating in hostile environments such as high-temperature and high radiation doses and under extreme conditions such as high frequency and high power. In particular, GaN and AlN form a continuous alloy system whose direct band gap at room temperature ranges from 3.4 to 6.2 eV, because of which their applications for many novel optical devices are very promising.

There has been a considerable amount of research effort directed towards the understanding of the optical properties of GaN and $Al_xGa_{1-x}N$. However, the dynamics of optical transitions, including the band-to-band, exciton, and band-to-impurity transitions in these materials, have never been investigated previously due to the lack of high-quality crystals and picosecond (or subnanosecond) laser spectroscopy systems with UV excitation and detection capabilities. Important basic quantities such as the recombination lifetimes of these optical transitions, which are crucial to the design of optoelectronic devices, have not yet been measured. With the recent advancement of epitaxial growth techniques, remarkable improvement in crystal quality has been achieved, especially for GaN. The investigations of the dynamic processes of optical transitions in these materials appear to be timely. In this letter, we report the first experimental investigation on the dynamic processes of band-edge optical transitions in GaN.

The GaN sample used here was grown by molecular beam epitaxy (MBE) on a sapphire (Al_2O_3) substrate with a 50 nm AlN buffer layer. The substrate temperature during the growth was 750 °C. An electron cyclotron resonance (ECR) source under a low microwave plasma power (70 W) provided the reactive nitrogen while Ga and Al were evaporated using conventional effusion cells. The thickness of the epitaxial layer was about 1 μm with room-temperature electron concentration of about 10^{17} cm^{-3} as determined by Hall measurements. An excitation pulse of about 7 ps at a repetition rate of 9.5 MHz was provided by a cavity-dumped dye laser, which was pumped by an yttrium–aluminum–garnet (YAG) laser with a frequency doubler. The output from the dye laser was frequency doubled again by a second frequency doubler to provide tunability in the UV region. The laser output after the second doubler has an average power of about 20 mW, a tunable photon energy up to 4.5 eV, and a spectral resolution of about 0.2 meV. A single photon counting detection system was used to record the time-resolved photoluminescence spectra. With the use of a deconvolution technique, the overall time resolution of the detection system was about 70 ps.

Figure 1 shows one representative continuous-wave (cw) spectrum of GaN measured at a temperature of 10 K, which shows two dominant emission lines. The full width at half-maximum (FWHM) of both lines is about 10 meV, which indicates that the sample under investigation is of high crystalline quality. The emission line at 3.474 eV is commonly believed to be due to the recombination of excitons bound to neutral donors (I_2).[6] The cw spectral peak position of the lower energy emission band varies from 3.414 to 3.422 eV depending on excitation intensity[7] and is very close to that of an emission band (at ~3.424 eV) associated with the presence of oxygen impurities reported in a previous literature by Chung *et al.*[8] There, the intensity of this emission band was found to be strongly dependent on the oxygen implantation dosage. The slight difference between the spectral peak positions observed in our sample and those of Chung's is most likely due to the following factors: (1) our picosecond pulsed laser has a lower pulsed power than that of the nitrogen laser used in the previous work; (2) samples used in the previous work have much higher impurity concentrations, because of which the emission bands were very broad. We assign the emission band near 3.420 eV observed here to the recombination between electrons bound to oxygen impurities and free holes (band-to-impurity transition), as proposed previously by Chung *et al.*[8] Other transition mechanisms, including donor–acceptor pair (DAP) recombination and the recombination between the free electrons and neutral acceptors, are less probable due to the following factors: (1)

[a]Permanent address: Department of Applied Physics, Xi'an Jiaotong University, People's Republic of China.

 0003-6951/95/66(25)/3474/3/$6.00

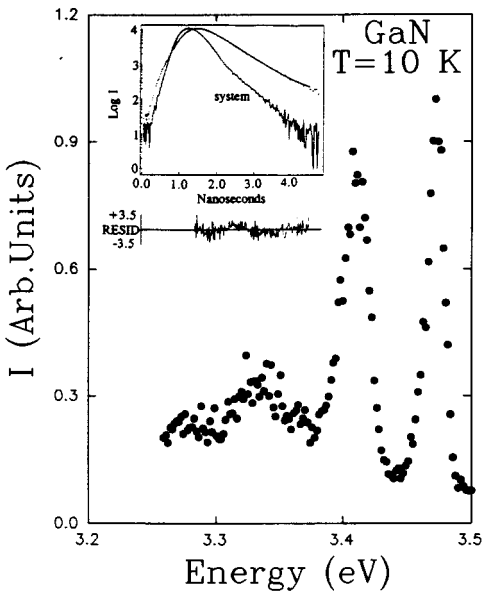

FIG. 1. One representative cw photoluminescence spectrum of GaN measured at $T=10$ K. The inset shows the semilogarithmic plot of the temporal response of the band-to-impurity transition measured at the peak energy and $T=10$ K. The instrument response to laser pulses (7 ps width) is indicated as "system" and the wiggling line is the experimental data. The solid line is the least-squares fit using a single exponential decay with the deconvolution of the instrumental response. The residues of the least-squares fit is also included at the bottom of the inset. Excitation energy was 4.260 eV.

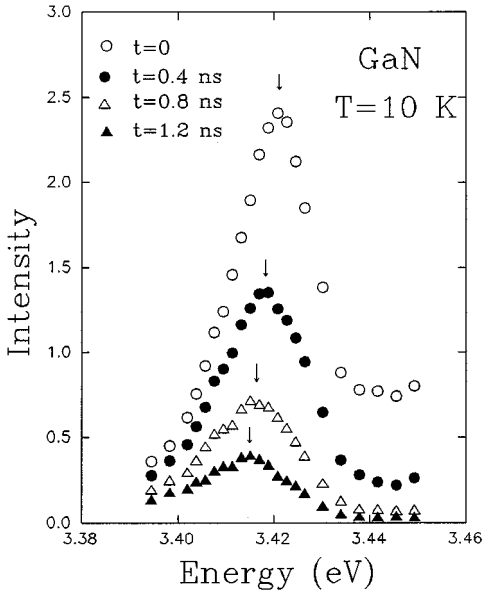

FIG. 2. Time-resolved photoluminescence spectra of the 3.42 eV emission line measured at $T=10$ K. The arrows indicate the spectral peak positions at different delay times. Delay time $t=0$ has been chosen at the positions of the maximum intensity in the luminescence temporal responses as shown in the inset of Fig. 1.

all known acceptor impurities in GaN have ionization energies which are too large to account for the energy position of this emission band, unless there exists an unidentified acceptor impurity with a smaller binding energy; (2) the known DAP zero-photon transition line in GaN occurs at about 3.26 eV;[6] (3) if the recombination of the short distant DAPs is responsible for the emission band near 3.42 eV, it would imply that the impurity concentration in our sample is very high, which is contrary to the Hall measurement result. Thus, our assignment for this emission line seems plausible.

Time-resolved emission spectroscopy has been employed to study the dynamics of the transition lines. In this letter, we are mainly concerned with the dynamic processes of the emission line near 3.420 eV. The inset of Fig. 1 shows a semilogarithmic plot of the temporal response of the transition line measured at the peak energy and $T=10$ K. As we can see the decay of this transition line in GaN is a single exponential, $I(t)=I_0e^{-t/\tau}$, with τ being the recombination lifetime. We have measured luminescence temporal responses such as that shown in the inset of Fig. 1 at different emission energies covering the entire emission band as well as at different temperatures from 10 to 150 K. In all cases, the decay of luminescence is single exponential.[7]

Figure 2 shows time-resolved emission spectra of the 3.42 eV emission line measured at $T=10$ K at several representative delay times. The arrows in Fig. 2 indicate the spectral peak positions at different delay times. Several features can be observed from Fig. 2. First, the peak positions of the emission line shift toward lower energies with an increase of delay time. Second, the linewidth of the emission line also increases with delay time. For a clear presentation, in Fig. 3 we have plotted the peak positions E_p and the full width at half-maximum (FWHM) of the emission line as functions of delay time. The peak position shifts toward lower energies linearly with delay time from 3.421 eV at $t=0$ to 3.414 eV at $t=1$ ns. The solid line in Fig. 3(a) is the least-squares fit of E_p by a linear equation, $E_p(t)=E_0-\alpha t$, and the fitted values are $E_0=3.421$ eV and $\alpha=5.88$ meV/ns. FWHM also increases linearly with delay time. The dotted line in Fig. 3(b) is the least-squares fit of FWHM with another linear equation, $\mathrm{FWHM}(t)=\mathrm{FWHM}(0)+\beta t$, and the fitted values are $\mathrm{FWHM}(0)=8.6$ meV and $\beta=2.66$ meV/ns.

The emission energy dependence of the recombination lifetime for the 3.42 eV transition line is depicted in Fig. 4, which shows that the lifetime (τ) is of the order of subnanoseconds and decreases with an increase of emission energy. In fact, the luminescence spectral shift with delay time as shown in Fig. 3(a) is a natural consequence of this strong emission energy dependence of the recombination lifetime. By approximating the emission line shape at the delay time $t=0$ by a Gaussian distribution, the time-resolved photoluminescence at emission energy E and delay time t can be written as

$$I(E,t)=I_0\exp\left\{-\frac{(E-E_0)^2}{2\sigma_0^2}-\frac{t}{\tau(E)}\right\}. \tag{1}$$

Here I_0 and E_0 are, respectively, the peak intensity of the luminescence and the spectral peak position at $t=0$. σ_0 is related to the FWHM at $t=0$ by $\mathrm{FWHM}=2[2(\ln 2)]^{1/2}\sigma_0$. The peak positions at different delay times can be obtained by setting $dI(E,t)/dE=0$, which gives

$$E_p(t)=E_0+\frac{\sigma_0^2}{\tau^2(E_p)}\left(\frac{d\tau}{dE}\right)_{E_p}t\ . \tag{2}$$

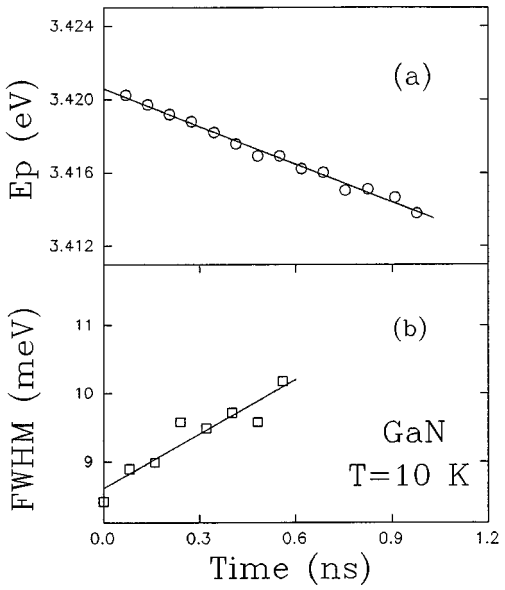

FIG. 3. (a) The peak positions E_p and (b) the full width at half-maximum (FWHM) of the 3.42 eV emission line as functions of delay time measured at $T=10$ K. The solid lines are the least-squares fits using $E_p(t)=E_p(0)-\alpha t$ and $\mathrm{FWHM}(T)=\mathrm{FWHM}(0)+\beta t$.

Based on the fact that τ decreases approximately linearly with E near E_p as shown in Fig. 4, and that the amount of E_p shift is much smaller than the impurity binding energy, we thus obtain,

$$E_p(t)=E_0-\alpha t. \tag{3}$$

This is what we have observed in Fig. 3(a).

If the band-to-impurity transition involves a single impurity energy level, the spectral shift with delay time and the variation of the recombination lifetime with emission energy are not expected. The results obtained here clearly indicate that the binding energy of the oxygen impurities in the sample under investigation has a distribution. There are two possible explanations for the emission energy dependence of the lifetime $\tau(E)$ as depicted in Fig. 4. First, the behavior is a direct consequence of the energy dependence of the radiative recombination rate, i.e., the behavior of $\tau(E)$ is associated with the distribution of the oxygen impurity binding energy E_b. This is based on the fact that the dependence of the radiative recombination lifetime of a band-to-impurity transition on E_b can be described by, $\tau \propto E_b^{3/2} \propto (E_g - h\nu)^{3/2}$, with $h\nu$ being the emission energy.[9] Therefore, a decrease in the recombination lifetime with an increase of emission energy is observed. The second possibility is the transfer of electrons from higher energy to lower energy sites among the impurities, which could happen for high impurity concentrations. The physical picture here would be analogous to the situation in II–VI semiconductor alloys,[10] in which excitons are localized in random potential wells induced by alloy disorder and can transfer from higher energy sites to lower energy sites by phonon emission. Here, photoexcited electrons could be localized in and thermally relax among different impurity sites with a relaxation rate that increases with an increase of emission energy.[10] In such a context, the observed lifetime behavior is primarily caused by nonradiative transfer. Our results seem to indicate that the behavior of $\tau(E)$ is caused by the former mechanism at 10 K.[7] However, the second possibility cannot be completely precluded, especially at higher temperatures.

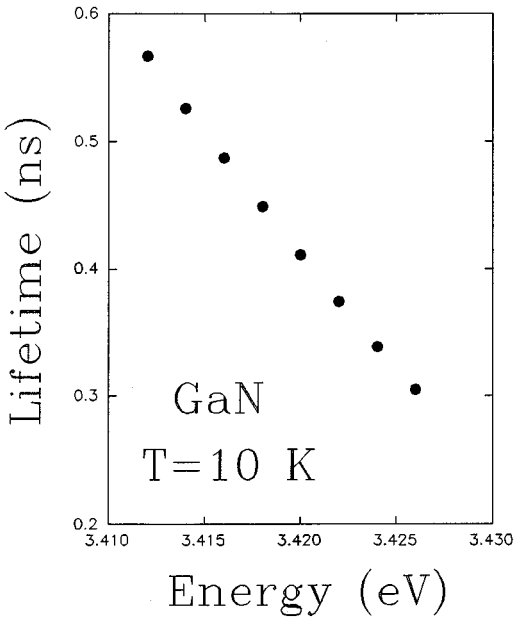

FIG. 4. Emission energy dependence of the recombination lifetime of the 3.42 eV emission line measured at $T=10$ K.

In conclusion, we have measured the time-resolved photoluminescence of a band-edge transition near 3.42 eV in a MBE grown GaN sample. An exponential decay behavior has been observed. The spectral shift with delay time has been shown to be a natural consequence of the observed emission energy dependence of the recombination lifetime, which is most likely due to the impurity binding energy dependence of the radiative recombination lifetime.

J.Y.L. and H.X.J. would like to thank Dr. John Zavada for his encouragements. A.S., B.N.S., A.B., and H.M. would like to acknowledge the support of the office of Naval Research under Grant No. N00014-89-J-1780 and thank Max Yoder for support.

[1] *Wide Bandgap Semiconductors*, edited by T. D. Moustakas, J. I. Pankove, and Y. Hamakawa, Mater. Res. Soc. Symp. Proc. 242 (MRS, Pittsburgh, 1992).
[2] S. Strite, M. E. Lin, and H. Morkoç, Thin Solid Films **231**, 197 (1993).
[3] J. I. Pankove, Mater. Res. Soc. Symp. Proc. **97**, 409 (1987).
[4] S. Nakamura, M. Senoh, and T. Mukai, Jpn. J. Appl. Phys. **32**, L8 (1993).
[5] M. A. Khan, A. Bhattarai, J. N. Kuznia, and D. T. Olson, Appl. Phys. Lett. **63**, 1214 (1993).
[6] S. Strite and H. Morkoç, J. Vac. Sci. Technol. B **10**, 1237 (1992).
[7] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang, A. Salvador, B. N. Sverdlov, A. Botchkarev, and H. Morkoç (unpublished).
[8] B. C. Chung and M. Gershenzon, J. Appl. Phys. **72**, 651 (1992).
[9] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), Chap. 6.
[10] H. X. Jiang, L. Q. Zu, and J. Y. Lin, Phys. Rev. B **42**, 7284 (1990).