Photocurrent decay in *n*-type GaN thin films

C. H. Qiu
Astralux Inc., 2500 Central Avenue, Boulder, Colorado 80301

W. Melton
Department of Electrical Engineering, University of Colorado, Boulder, Colorado 80309-0425

M. W. Leksono and J. I. Pankove
Astralux, Inc., 2500 Central Avenue, Boulder, Colorado 80301

B. P. Keller and S. P. DenBaars
Electrical and Computer Engineering and Materials Departments, University of California, Santa Barbara, California 93106

(Received 8 April 1996; accepted for publication 18 June 1996)

Minority carrier relaxation in undoped *n*-type gallium nitride (GaN) thin films was studied by photoconductivity decay measurements in the time span from 50 ns to 50 s. The decay is characterized by an initial exponential decay followed by a quasi-power-law decay for decades of time longer than 1 μs. The decay rate is insensitive to the electron concentration and is only slightly temperature dependent. The results are discussed in terms of hole trapping at gap states and subsequent recombination. The studies revealed that the dominant recombination mechanism is very different from recombination through dislocations and that the valence band-tail states in *n*-type GaN seem to be negatively charged. *© 1996 American Institute of Physics.* [S0003-6951(96)05035-8]

Gallium nitride (GaN) and its alloys with Al and In are important candidate materials for blue-UV lasers, short wavelength radiation detectors, and high-temperature electronics. This is evident from several impressive device achievements in the last few years, including the injection light-emitting diodes (LED),[1–4] laser diode,[5] solar-blind UV detectors,[6,7] and high-temperature transistors.[8,9] However, recent studies revealed high densities of structural and electronic defects in nitride semiconductors. A high density of dislocation was observed in the blue LEDs of Nichia,[10] while a broad distribution of states within the forbidden gap of GaN is revealed by both photoconductivity spectroscopy[11] and photothermal deflection spectroscopy.[12] Photoluminescence decay measurements by several groups yielded *sample-dependent* lifetimes of the free excitons and bound excitons,[13–15] probably due to trapping at gap states. There are very few reports on the nature of the gap states and on their possible role in minority carrier relaxation. Since the minority carrier relaxation is an important process in device operation, we performed photoconductivity decay studies of GaN films grown by metalorganic chemical vapor deposition (MOCVD). In contrast to photoluminescence decay, photoconductivity decay is a perfect tool to measure the *total* decay rate of nonequilibrium carriers. In this letter, we present results on undoped *n*-type GaN. The studies revealed that the dominant recombination mechanism in *n*-type GaN is very different from recombination through dislocations and that the gap states seem to be negatively charged.

The undoped *n*-type GaN thin films were grown on *c*-plane sapphire at Astralux in two cold-wall low-pressure MOCVD systems and a hot-wall atmospheric pressure MOCVD system. We have measured over two dozen undoped GaN films with electron concentrations in the range of $9\times10^{16}-1.3\times10^{19}$ cm^{-3}. The electron mobility at room temperature is in the range of 73–450 cm^2/V s. To make sure that the measured data are of general relevance, sample ''SB''in this letter was a high quality GaN film grown at the University of California, Santa Barbara, using atmospheric pressure MOCVD.[16] The photoconductivity was excited by a pulsed nitrogen laser at 337 nm (PTI Inc. Model PL2300),[17] and was measured in a coplanar geometry with two indium contacts soldered to the GaN surface. The gap between the electrodes was about 1 mm. A dc voltage was applied to the sample through a series resistor. The dc voltage and the series resistor were chosen to minimize sample self-heating. The voltage output from across either the sample or the load resistor, the one with the smaller resistance, was measured with a Tektronix 11403 Digitizing Oscilloscope and recorded by a computer. The RC time constant of each measurement circuit was less than 1 ns. In other words, the experimental setup is similar to that used by Stevenson and Keyes for measuring minority carrier lifetime.[18] For temperature-dependent decay measurement, the samples were placed on a cold finger inside a Dewar equipped with a closed cycle helium refrigerator.

For the photoconductivity decay measurement of most samples, the voltage across the electrodes was less than 1 V. Essentially identical decay curves (within our measurement accuracy) were observed by using a 10 times higher applied voltage. Figure 1 shows the photoconductivity decay at room temperature for several selected samples. The photoconductivity was excited by an unfocused laser beam, with an intensity of ~20 kW/cm^2 and a pulse width of 10 ns. Identical decay curves were obtained when the light intensity was reduced by over four orders of magnitude, except that the photoconductivity at any given decay time was found to be a sublinear function of the laser intensity. The data in Fig. 1 are plotted in a log–log scale. A straight line in such a plot implies a decay governed by a power law, $\Delta n = At^{-\alpha}$. In the time span of ~1 μs–0.1 s, the exponent α for all the samples

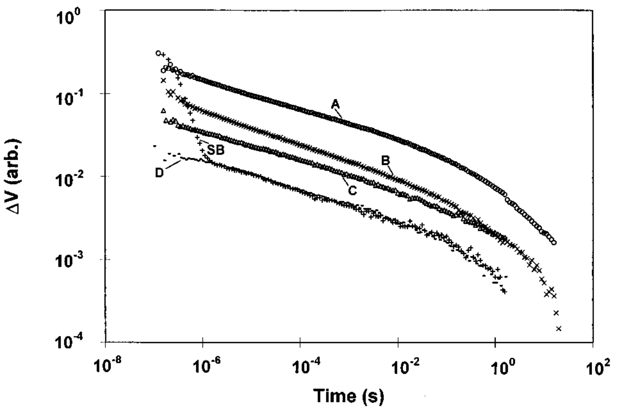

FIG. 1. Photoconductivity decay of *n*-type GaN measured at room temperature for samples with electron concentration of (A) 9.6×10^{16} cm^{-3}, (B) 5×10^{17} cm^{-3}, (SB) 3.4×10^{17} cm^{-3}, (C) 1.3×10^{18} cm^{-3}, and (D) 1.3×10^{19} cm^{-3}.

we measured was almost the same, with an average of 0.193 and a standard deviation of 0.011. In a semilog plot of $\log(\Delta V)$ versus time, photoconductivity data at $t<0.5$ μs for a few samples were approximately linear with a sample-dependent time constant in the range of 0.2–0.8 μs. In other words, the photoconductivity decay is approximately exponential at short times ($t<0.5$ μs) and generally does not follow the simple exponential for decades of time ranging from 10^{-6} to over 10 s.

We note here that the decay result can hardly be explained by laser induced heating and subsequent cooling. One can estimate an upper limit for the temperature increase due to laser absorption by assuming that the incident laser is totally absorbed in an absorption depth $1/\alpha$, which is about 125 Å at $\lambda=337$ nm.[19] For a GaN film, the upper limit of the temperature increase is expected to be 54 °C, by using a density ρ of 6.09 g/cm^3 and a heat capacity C_p of 0.487 J/g K near room temperature. If the film thickness is d, the heat would conduct through the sample with a time scale of $\tau=4d^2/D\pi^2$, where D is determined by thermal conductivity K through $D=K/\rho\ C_p$. In other words, for a 1 μm thick GaN film, the temperature increase due to laser absorption will be less than 1 °C in a time of about 10 ns ($K=1.3$ W/cm K at room temperature,[20] τ is about 10 ns for $d=1$ μm). This increase in temperature is too small to explain the observed change in resistivity.

In the following, we would like to provide some framework for the discussion of the photoconductivity decay data. For *n*-type GaN, photoconductivity spectra measurements indicated a broad tail of states extending from the valence band edge into the forbidden gap.[11] Thus, the nonequilibrium holes produced by photoexcitation are expected to be rapidly trapped into such gap states, and as a result, only the photogenerated electrons are expected to contribute to photoconductivity. For the electron concentration covered in this study (10^{16}–10^{19} cm^{-3} at room temperature), the electron Fermi level is very close to the conduction band edge. For every trapped hole, there is approximately one electron above the Fermi level that contributes to the observed photoconductivity. Thus, the photoconductivity observed 10 s after the laser pulse implies that some holes are trapped in gap states for 10 s or longer. In other words, the photoconductivity decay is a measure of the relaxation of trapped holes.

The initial exponential decay exhibited a time constant of 0.2–0.8 μs, which did not seem to correlate with the electron concentration. The time constant is also considerably longer than the expected minority carrier lifetime estimated from Hall's formula.[21] We suggest that the initial exponential decay is an indication of discrete shallow hole traps.

One striking result of Fig. 1 is that the observed photoconductivity decay rate at $t>1$ μs is similar for samples with very different electron concentrations. This result is distinctly different from the quasi-power-law photoluminescence decay arising from donor–acceptor pair (DAP) recombination. According to Thomas *et al.*, the exponent of the quasi-power-law decay in DAP recombination depends rather sensitively on the concentration of donors and acceptors.[22] Thus, the recombination of the trapped holes with electrons in donor sites does not seem to be a dominant recombination mechanism for *n*-type GaN at room temperature.

The same data also suggested that the trapped holes are unlikely to recombine directly with electrons in the conduction band through electron capture. In other words, the electron capture-cross section of the gap states seems to be very small. If the free-electron capture by the trapped holes was an important recombination channel, one would expect a decay rate dependent on the electron concentration. We shall estimate in the following an upper limit for the electron capture-cross section. Our data indicated that the trapped holes can ''live'' for 1 μs or longer even for highly degenerate *n*-type GaN (electron concentration $n>10^{19}$ cm^{-3}). In other words, $1/(nvS_n)>10^{-6}$ s, where $v=10^7$ cm/s is the average thermal velocity of electrons, and S_n is the electron capture-cross section of a gap state at which a hole is already trapped. Thus, $S_n<10^{-20}$ cm^2. Such a small electron capture-cross section usually corresponds to negatively charged centers.[23] We speculate that this result may be evidence for Ga vacancies suggested by several theoretical calculations.[24]

The quasi-power-law decay is suggestive of the relaxation of trapped holes through thermal excitation to the valence band followed by recombination with electrons in the conduction band. When the density of states in the valence band tail can be represented by an exponential distribution as $N_t\exp(-E/E_0)$, the exponent α is expected to be temperature dependent and is given by kT/E_0,[25] where k is the Boltzmann constant. We thus measured the photoconductivity decay at several temperatures in the range from 6 to 390 K. For clarity, only four decay curves are plotted in Fig. 2(a), and the exponent α is plotted in Fig. 2(b). Below 200 K, the decay curve is almost independent of temperature. Above 200 K, the exponent increases with temperature, indicating faster decay at higher temperatures. A least-square linear fit of the α vs T data yields a slope of $E_0=190$ mV. This E_0 value agrees rather well with that obtained from the photoconductivity spectrum of the same sample measured at room temperature, which is $E_0=180$ meV for photon energies from 1.5 to 3.1 eV corresponding to deep gap states. However, further studies are needed to establish the generality of

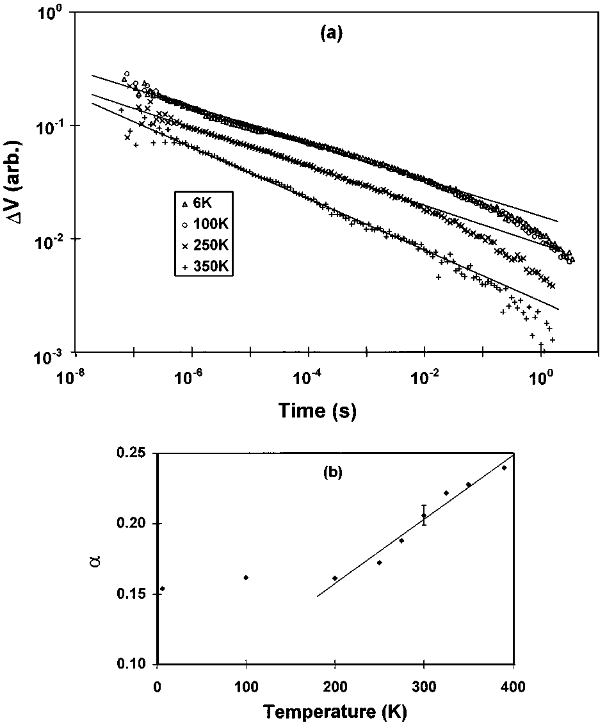

FIG. 2. (a) Photoconductivity decay of an *n*-type GaN at several temperatures. The electron concentration at room temperature is 2.2×10^{18} cm^{-3}. (b) The exponent α obtained from the quasi-power-law decay as a function of temperature. The line represents the least-square linear fit for data at $T>200$ K.

this agreement, and the low-temperature constant term in α is not understood either.

The quasi-power-law decay may also be explained by tunneling of the trapped hole to a defect center, such as the center giving rise to the yellow luminescence, where it recombines with an electron from the conduction band. According to Thomas *et al.*, the exponent α is expected to be insensitive to sample differences if the density of such centers is about the same for all the samples.[22] For the films we studied, the intensity ratio of the edge luminescence to the yellow luminescence is between 1.5 and 6 at room temperature, indicating a comparable density of the centers giving rise to the yellow luminescence.

It is clear, however, that the observed photoconductivity decay is very different from that controlled by recombination through dislocations.[26] Furthermore, the steady state photoconductivity for across the gap photoexcitation increases with increasing temperature,[27] in contrast to the thermal quenching behavior observed for recombination at dislocations. It thus seems that recombination at dislocations is not a dominant recombination channel in undoped *n*-type GaN.

In summary, we studied the photoconductivity decay of undoped *n*-type GaN films. The decay is characterized by an initial exponential decay followed by a quasi-power-law decay for decades of time longer than 1 μs. The decay rate is insensitive to the electron concentration and is slightly temperature dependent. The minority carrier relaxation in *n*-type GaN is controlled by trapping at gap states. The trapped holes most probably dissipate through thermal excitation to the valence band followed by direct recombination and through tunneling to the defect centers that give rise to the yellow luminescence.

The authors thank Professor Kathy Rowlen for lending the nitrogen laser, Professor Ted Moustakas for helpful discussions during the early stage of the work, and C. Hoggatt for Hall effect measurement. The work at Astralux was supported in part by DOE Grant DE-FG03-95ER86024, and monitored by Dr. R. Rinkenberger. W. Melton was supported by ARPA-URI Grant N00014-92-1-1895.

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