Time-resolved photoluminescence studies of free and donor-bound exciton in GaN grown by hydride vapor phase epitaxy

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Time-resolved photoluminescence spectroscopy was used to study the radiative recombination of free and donor-bound excitons in unintentionally doped GaN grown by hydride vapor phase epitaxy. Low temperature (4 K), time-integrated PL spectra identified the free exciton (A), the donor-bound exciton peak ~6 meV below, and the acceptor-bound exciton ~20 meV below the free exciton peak. A radiative recombination lifetime of 295 ps for the free exciton and 530 ps for donor-bound exciton were found at 4 K. The decay of the free exciton remained single exponential to room temperature, with an increase in lifetime to 530 ps, consistent with the thermal excitation of exciton states.

GaN and its alloys (AlGaN and InGaN) are considered to be some of the most promising materials for the fabrication of blue-green[1] and UV light emitting diodes (LED's), laser diodes (LD's), UV solar blind detectors and high power/high temperature electronics. GaN films of good optical quality grown on sapphire substrates by molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) have been reported in recent years.[2,3,4,5] Recently, significant progress in growing high quality hydride vapor phase epitaxy (HVPE) material has been achieved.[6] The high growth rates (up to ~100 μm/h [7]) make possible thick layers, providing an inexpensive alternative substrate for GaN epilayers, and thus generating considerable interest in HVPE material.

A clear understanding of recombination mechanisms at room temperature is especially important for optoelectronics applications. Time-resolved photoluminescence (TRPL) is a powerful experimental tool to study new materials because the temporal information combined with spectral data can help determine the dynamics of carriers involved in optical processes. In this letter we present the results of time-resolved studies of exciton luminescence in single crystal GaN films grown on sapphire substrates by HVPE.

Previous measurements of the exciton lifetime have been dominated by multilevel processes yielding biexponential decays and large variations in decay rates as a function of temperature.[8-11] In contrast, our data display single exponential decays over several times the radiative recombination lifetime, and a temperature dependence simply understood as the thermal population of excited exciton states. Radiative recombination lifetime for free excitons of 375 ps at 60 K has been reported by S. Hess, *et al*. [8] in lateral overgrowth metal-organic vapor phase epitaxy (MOVPE) material. Their data at 60K is fit by a biexponential decay, characteristic of multiple capture processes. At 4 K their free exciton time resolved data are fitted with a single exponential decay with a time constant of 16 ps. On the other hand, a free A exciton lifetime of 66 ps at 4 K and donor bound exciton (D^0X) lifetime of 136 ps have been reported by S. Pau, *et al*.[9] in MOCVD material. The radiative recombination lifetime of the donor bound exciton (I_2 transition) reported so far varies from 30-100 ps[10] to 250 ps at 4 K.[11] In comparison, we report a radiative recombination lifetime of 295 ps at 4 K and 530 ps at room temperature (RT) for the free A exciton, and of 530 ps at 4 K for the D^0X. The lifetime is obtained by a least squares fit of the data to a single exponential decay.

The experiments are carried out on a 63 μm thick GaN film grown on a (0001) sapphire substrate by HVPE. The growth technique employs a chloride-transport HVPE vertical reactor, with growth rate ~21 μm/h at 1050 ºC, which results in unintentionally doped GaN with a room temperature electron concentration of ~ $6x10^{16}$ cm^{-3} and mobility of 820 cm^2/Vs, as determined by Hall effect measurements. Time-resolved photoluminescence measurements are performed using a pulsed picosecond mode-locked Ti:sapphire laser (1.5 ps pulse width) and a microchannel plate photomultiplier tube (MCPMT). The laser pulses are frequency-doubled resulting in an excitation wavelength of 352 nm. The repetition rate is changed to 13.66 MHz using a Pockel cell. The average power is 40 mW and the typical diameter of the laser spot on the sample is ~100 μm. The emitted light is dispersed by 0.64m spectrometer and collected onto the photocathode of the MCPMT. The PL data are recorded by a cooled charge coupled devices (CCD) array. The spectral resolution is 0.6 Å and the overall temporal resolution of the system is less than 65 ps. The sample temperature is varied from 4-300 K using a flow-through helium cryostat.

The near band edge time-integrated photoluminescence (PL) at 4 K is presented in Figure 1. The spectra is dominated by donor-bound exciton peak at ~3.47 eV. The full width of half-maximum (FWHM) of 1.9 meV is consistent with other reports of high quality GaN grown on sapphire. [4, 9] A shoulder on the high-energy side of the I_2 transition can be distinguished, which is associated with the

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free A exciton (FX). The energy for FX, obtained by fitting Lorentzians to the spectra, is ~3.476 eV. This yields a binding energy of 6 meV for D^0X, in agreement with other measurements.[12] The peak at ~3.45 eV has been attributed to acceptor bound exciton.[13, 14] The peak at 3.378 eV is a LO phonon replica of the I_2 line. The shoulder at 3.388 eV has been attributed to either LO phonon replica of the free A exciton[15] or free to bound transition of a 116 meV impurity.[16, 17]

In Fig.1, the inset shows the linear time-integrated spectra at room temperature. The peak at 3.4 eV is due to the free exciton (FX) recombination. The spectral shape featuring a low energy shoulder has been attributed in literature to strong reabsorption at ~ 3.37 eV.[18,19] No significant change in the PL spectra is observed when we decrease the excitation intensity by four orders of magnitude, indicating that no band-gap filling or saturation of the defect-related level effects are present.

Time resolved spectra of the FX and D^0X at 4 K are presented in Fig.2. The FX time response remains single exponential decay for over 1ns; the solid line represents a single exponential fit with a time constant of 295 ps. In bulk semiconductors the radiative decay of free excitons requires scattering to the photonic region of the polariton dispersion branch, and thus the radiative lifetime is determined by the time necessary to pass through the excitonic polariton bottleneck region.[8] In the absence of defects, a theoretical analysis by Toyozawa[8] yields a radiative lifetime of t_{rad} ~300 ps for the free exciton A in GaN. The theoretical lifetime is in excellent agreement with our experimental results. This, along with the single exponential decay of the data, indicate that we have a very small number of defect levels in the sample or that their relaxation time is very long, in contrast to previous reports.[8, 9, 11, 20]

Time resolved spectra of D^0X are also fit by a single exponential decay over 1.7 ns; the radiative recombination lifetime is found to be 530 ps. The radiative lifetime for an excited state in a semiconductor can be estimated from consideration of the optical transition probability: [21,22]

$$t_{rad} = \frac{2pe_0 m_0 c^3}{ne^2 w^2 f} \qquad (1)$$

where *f* is the oscillator strength of the optical transition, and n is the refractive index. By using n=2.67 [23] and ? =5.28x10^{15} s^{-1} for GaN one can estimate t_{rad} ~ 690/f ps. Our experimental results indicate an oscillator strength of ~1.3, close to the theoretical value f ~ 1.[23] A radiative recombination lifetime of ~ 300 ps for D^0X exciton was measured for a sample grown by HVPE under similar conditions. [24]

We also studied PL as a function of temperature. For T>100K the spectra are dominated by free excitons. This is due to the ionization of the donor bound exciton (D^0X => D^0+X). No peak associated with band-to-band transition at energies ~26 meV above the FX peak was observed, indicating that the recombination mechanism is dominated by the FX, even at room temperature.

Radiative recombination lifetime of excitons has been particularly difficult to obtain at room temperature, due to nonradiative recombination centers which capture the carriers rapidly yielding very short lifetime values. Time resolved spectra at RT for FX is presented in Fig.3. The solid line represents a single exponential decay fit with a time constant of ~530 ps. The radiative lifetime of FX increases from ~295 ps at 4 K to ~530 ps at RT. The influence of the lattice temperature on the radiative lifetime of the free excitons can be explained simply in terms of an increase in the center of mass kinetic energy. For low excitation intensity the free excitons behave as a Maxwell-Boltzmann distribution. Therefore, the number of free excitons decreases as lattice temperature increases, and hence the radiative recombination lifetime increases with T.[23]

In conclusion, we have presented TRPL measurements of free and donor bound excitons in GaN crystals grown by HVPE. A radiative recombination lifetime of 295 ps at 4K is found for the free A exciton, in agreement with a theoretical analysis which neglects the role of dislocations. The free exciton lifetime increases to 530 ps at room temperature, consistent with thermal population of excited states. The D^0X exciton radiative lifetime is 530 ps at 4 K, which yields an oscillator strength of ~1.3. The lifetimes are obtained by single exponential decay fits of the data, which indicate that no effects due to nonradiative recombination centers (characterized by very short decay time) are present in the material. We note that as the quality of the sample improves, picosecond time resolved PL becomes a powerful method to investigate the spontaneous emission mechanisms in bulk GaN.

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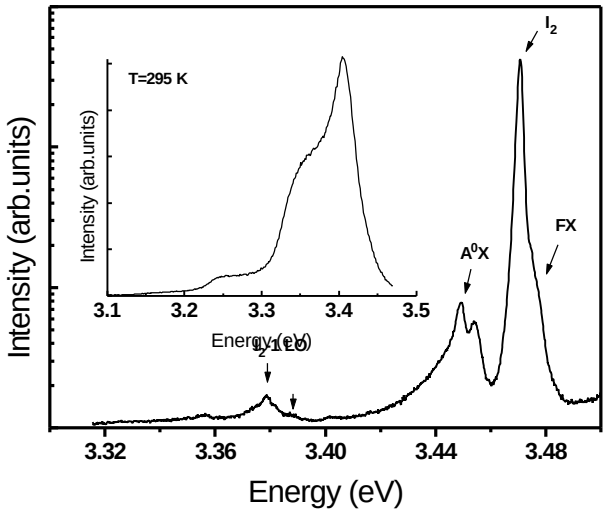

FIG.1. Time-integrated photoluminescence at 4 K (log-linear scale) and room temperature (linear-linear scale).

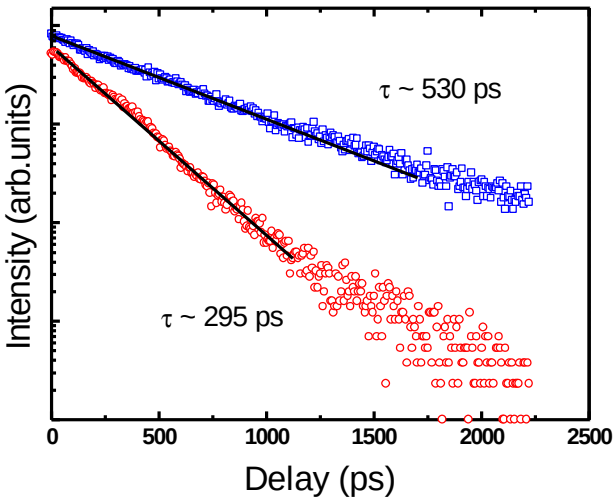

FIG.2. Time-resolved photoluminescence spectra at 4 K (log-linear scale). The square represents the data for free excitons and the circle represents the donor bound exciton. The solid lines are single exponential fits to the data.

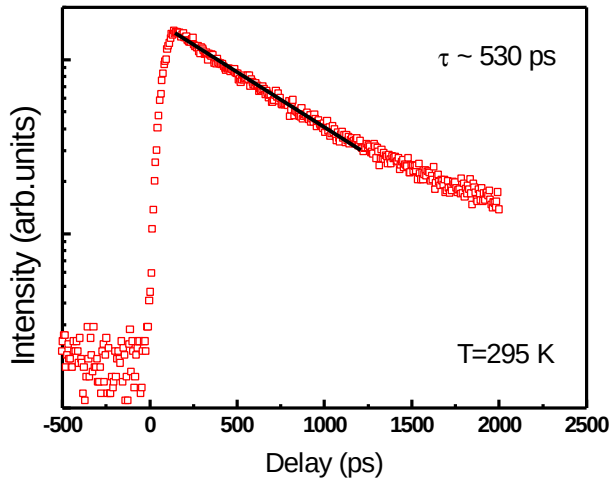

FIG.3. Time-resolved results for free excitons at room temperature (log-linear scale). The solid line is a single exponential fit to the data.

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