FINE STRUCTURE OF THE 3.42 eV EMISSION BAND IN GaN

S. FISCHER*, C. WETZEL, W. WALUKIEWICZ, and E.E. HALLER

Lawrence Berkeley National Laboratory and University of California, Berkeley, CA 94720, USA

ABSTRACT

A luminescence band centered around 3.42 eV is commonly observed in GaN. Its appearance has been tentatively assigned to an oxygen donor level. Stimulated laser activity has also been reported at this energy. We present a study of this band in GaN grown by high temperature vapor phase epitaxy (HTVPE). The high quality of this material, with an excitonic line width as narrow as 3 meV, allows us to distinguish four different peak positions of this luminescence band. They appear at 3.4066, 3.4121, 3.4186, and 3.4238 eV ($T = 6$ K). Within the experimental error the lines exhibit an equidistant spacing of 6 meV. They show a pressure behavior similar to shallow levels described by effective mass theory. We discuss our results in the context of incorporation of oxygen and structural defects in GaN.

INTRODUCTION

The strong commercial interest for the group-III nitrides is primarily based on its application in light emitting devices. A characterization of the materials properties by photoluminescence (PL), however, is not just a natural consequence, but in addition can provide detailed information on the recombination processes involved. So far several characteristic luminescence bands have been described in GaN which can be attributed to one of the following: Transitions between shallow bound carriers in the vicinity of the bandgap, transitions in the blue-violet spectral range involving an acceptor level and a broad band in the yellow part of the visible spectrum of as yet unidentified origin. In addition a strong band centered around 3.42 eV is frequently observed in low temperature PL spectra of GaN [1-8]. Lying energetically between the transitions of shallow bound carriers and acceptor related transitions this band recently attracted considerable interest. Several groups have reported stimulated emission at this photon energy in optically pumped GaN. Laser activity was observed at 3.424 eV (10 K) [9] and 3.43 eV (77 K) [10]. These values coincide with the 3.42 eV band described here. In those reports, however, no explanation could be given on the origin of this transition. In PL studies this transition has been found in GaN powder [2,5,7], single crystal needles [1], as well as in epitaxial films on sapphire (HVPE [4,6], MBE [3] and MOCVD [8]). The reported peak energy vary between 3.41 and 3.435 eV. The appearance of this band could not be correlated to special conditions of the growth processes in these reports.

It has been reported that doping of GaN by incorporation of C [5], Hg or Li [7] in the Ga melt produces or enhances this emission. In a very recent report, however, it was found that both, injection of H₂O during MOCVD growth, or implantation of O can produce this PL band (3.424 eV) [8]. In the same work it was found that implantation of O in HVPE material produced this band at 3.415 or 3.424 eV and it was assigned to a donor to valence band (D^0h) transition involving a 78 meV deep O related donor level. The observed PL features were broad and no fine structure could be resolved most likely due to the high n-type conductivity [8].

In a study of this band by time resolved PL a wide distribution of recombination life times was found. The peak energy ranged between 3.414 and 3.422 eV in these MBE grown samples. From the distribution of the life times found incorporation of several levels in this transition was concluded. But again, no fine structure in standard, time integrated, PL could be found [3].

We present data of various GaN samples resolving up to four different peaks contributing to the 3.42 eV band.

EXPERIMENTAL

Nominal undoped GaN films were grown by High Temperature Vapor Phase Epitaxy (HTVPE). In this unconventional growth technique liquid Ga and NH_3 act as Ga and N sources. No transport gas is necessary. Growth onto various substrates was performed at a temperature of 1200 - 1240°C. GaN was grown either on sapphire (c- and r-plane), 6H-SiC (c-plane) or directly onto the graphite crucible. Highly oriented films at thicknesses up to 20 nm were obtained on the substrates, whereelse growth by nucleation on the graphite resulted in microcrystalline grains (typically 100 nm in diameter). The best crystalline quality was achieved on SiC substrates as shown by x-ray rocking curve measurements. More details are given in Ref. [11].

PL was performed at both low temperature (6 K) and temperature dependent (6 K-300 K). The luminescence was excited with the 325 nm line of a 10 mW HeCd Laser. The emitted light was dispersed by a 0.85 m double monochromator and detected by a UV sensitive photomultiplier using lock-in technique. Additional hydrostatic pressure was applied by means of a Merrill-Bassett type diamond anvil cell. The fluorescence of the R_1 ruby lines at 6 K was used for pressure determination [12].

RESULTS

A typical PL spectrum at 6 K of GaN/6H-SiC and GaN/sapphire films is presented in Fig. 1. For GaN/6H-SiC the PL is dominated by the donor bound exciton (D^0X). At lower energies clearly resolved band-acceptor (eA) and donor-acceptor (DA) transitions between the residual donor and carbon acceptor are present [13]. In this material no contribution can be found in the vicinity of 3.42 eV. The energetic distance between the DA and eA transitions can be used to determine the free carrier concentration by an interpretation of the coulomb shift. The derived concentrations are in the high 10^{16} and low 10^{17} cm^{-3} for the GaN on 6H-SiC films. For GaN/sapphire the PL is also dominated by the D^0X . However, a second prominent emission is the band found at 3.42 eV. At lower energies in the range of the acceptor related transitions, an eA, but no DA transition is observed. This indicates a rather high carrier concentration above $n = 1 \times 10^{18} \text{ cm}^{-3}$ [13]. The PL of small substrate-free grown crystals is very similar to the spectrum of GaN on sapphire.

Fig. 1: Representative PL spectra of GaN films grown on sapphire and 6H-SiC. Both are dominated by the donor bound exciton at 3.472 eV. The striking feature is the appearance of a strong 3.42 eV luminescence in the film grown on sapphire.

The peak position of the 3.42 eV band varies within different samples of the HTVPE material. We are able to resolve four distinct peak positions. They appear at 3.4066, 3.4121, 3.4186, and 3.4238 ± 0.002 eV and are named furtheron L1, L2, L3, and L4, respectively (see Fig. 2). For all of those samples we find the identical value of the D^0X line at 3.4715 ± 0.0019 eV. This value is very close to the energy observed in bulk material [14]. This indicates that all films are already relaxed and no residual stress is present. This therefore rules out any stress effect that could have let to a splitting of a single transition at 3.42 eV. Therefore we find optical binding energies of 96.4, 90.9, 84.4, and 79.2 meV with respect to the bandgap of GaN (3.503 eV at 6K [15]).

It is seen in Fig. 2 that L1 - L3 appear as the dominant emissions in the PL spectrum. However this behavior is only observed on samples grown on sapphire, where the growth process was stopped before the entire substrate area was covered. In this case the full width at half maximum (FWHM) of the L1 - L3 lines is below 30 meV and as low as 14.1 meV. If the (D^0X) is the dominant emission the FWHM of the lines L1 - L4 is above 30 meV and as broad as 60 meV. This gives rise to the assumption that the broad emissions contain contributions of their adjacent lines. Additionally a weak 3.42 eV luminescence is found in GaN films grown on 6H-SiC of lower crystalline quality exhibiting a cracked surface.

Fig. 2: Normalized PL spectra of different samples showing the four distinct peak positions of the 3.42 eV band. The peaks are named L1, L2, L3, and L4 with peak energies of 3.4066, 3.4121, 3.4186, and 3.4238 eV, respectively. The peak at higher energy is the donor-bound exciton ($D^{\circ}X$).

In order to investigate the origin of these recombinations temperature dependent PL was performed on a sample with a peak emission at L3. From 6 to 40 K L3 shifts to higher energies with a slope of 0.21 meV/K. Above 40 K it shifts to lower energies almost simultaneously with the ($D^{\circ}X$), see Fig. 3. Contrary to another report both emissions can be well separated above 80 K and even resolved at 300 K. From the thermal quenching a activation energy of the L3 line of $E_A = 19 \pm 2$ meV is determined.

Additional hydrostatic pressure up to 1.7 GPa was applied to the small GaN crystals exhibiting the same PL as the GaN films grown on sapphire. The 3.42 eV emission was again on the L3 position. Under increasing hydrostatic pressure L3 shifts towards higher energies parallel to the ($D^{\circ}X$). We find a linear pressure dependence for both, the L3 line and the ($D^{\circ}X$), similar to a recently determined one in an AlGaIn/GaN/sapphire sample for the ($D^{\circ}X$) of the GaN layer [16].

DISCUSSION

We will mainly discuss the L3 level under the assumption that L1, L2, and L4 show a similar behavior.

Fig. 3: The luminescence of the L3 line is shown as a function of temperature. From 6 to 40 K L3 shifts to higher energies. Above 40 K it decreases in energy simultaneously to the (D^0X). This temperature dependence is typical for a free-to-bound transition.

The shift to higher energies with increasing temperature is typical for a free to bound transition. This shift can be attributed to an increase in the mean velocity of holes in the valence band of a (D^0h) transition. In this case the thermal activation reveals the involved donor. One has to keep in mind that in n-type material the Fermi level lies approximately in the middle between the dominant shallow donor level and the conduction band (CB). Only half of the donor binding energy is therefore necessary to excite electrons from the Fermi level to the CB. This would indicate that a donor level 38 meV below the CB is involved, which is within the experimental error the residual donor in GaN ($ED = 35.5$ meV [17]). The activation energy and the residual donor level depth are significantly lower than the determined level position of 85 meV below the CB. Also the appearance of four different peak positions can not be explained within the simple (D^0h) model.

On the other hand the pressure dependent measurement showed that the level shifts parallel to the bandgap. This is the expected behavior for a hydrogenic level which can be described by effective mass theory. Therefore deep localized levels can be excluded.

In general in GaN films grown on sapphire an one order of magnitude higher carrier concentrations compared to the films grown on 6H-SiC is observed. High resolution transmission electron microscopy reveals that the sapphire substrate is significantly affected at the growth temperature in contrast to 6H-SiC [18]. Thus a release of O from the substrate and a doping of the GaN film is possible. In Ref. [8] injection of H_2O during growth lead to higher

carrier concentrations, which was attributed to an additional incorporation of O donors. O is also a candidate for the residual donor in GaN [19], whereas as shown above the residual donor level is much shallower than the L1 - L4 levels.

However the following has to be taken into account. On GaN/SiC samples of lower structural quality a weak 3.42 eV luminescence can be observed. Additionally the microcrystalline GaN exhibit the same PL as GaN on sapphire. In both, the microcrystalline GaN and the films grown on sapphire much more structural defects are observed than in the GaN films grown on 6H-SiC [18]. This seems to be obvious considering the larger lattice mismatch of sapphire compared to 6H-SiC or the random nucleation on the crucible. Therefore one also has to consider structural defects to be responsible for the L1 - L4 lines. This could explain the observations in other publications where the 3.42 eV band vanished in the films of higher structural quality [4,6].

To summarize we have found four distinct peak position of the 3.42 eV band, named L1, L2, L3, and L4, at 3.4066, 3.4121, 3.4186, and 3.4238 eV, respectively. Under hydrostatic pressure the respective levels shift like shallow hydrogenic levels parallel to the bandgap. Temperature dependent PL measurements show a shift towards higher energies as expected for a (D^0h) transition. However the revealed thermal activation energy is much lower than the corresponding energetic position of the respective level.

Besides the believed involvement of a O related donor level in these transitions [8] there is experimental evidence for structural defects playing a major role.

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* current address: Physik Department E16, Technical University Munich, 85747 Garching, Germany

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