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Properties of the yellow luminescence in undoped GaN epitaxial layers

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Photoluminescence, time-integrated, time-resolved, and photoluminescence excitation spectroscopy have been employed to study the 2.2 eV ("yellow") emission in undoped GaN epitaxial layers. It is best described by a recombination model involving shallow donors and deep donors of probably intrinsic origin. Optically detected magnetic resonance reveals the participation of the shallow donor based on the analysis of the g value and Lorentzian line shape.

I. INTRODUCTION

In order to explain the origin of the inherent n-type conductivity of undoped GaN, defect models involving intrinsic defects such as vacancies and interstitials are commonly debated.[1–3] Anion vacancies or interstitials can act as multiple donors and are expected to introduce deep levels in the bandgap of the semiconductors. It was therefore appealing to consider those defects as a source for the omnipresent 2.2 eV photoluminescence (PL) band in undoped GaN. Indeed, in recent investigations the signals observed by optically detected magnetic resonance (ODMR) on the 2.2 eV PL in undoped GaN epitaxial layers were attributed to shallow donors and deep donors, the latter likely to be caused by an intrinsic defect.[4–6] In the most recent investigation the recombination mechanism for the 2.2 eV PL was explained by a recombination from a deep intrinsic double donor to shallow acceptors.[6]

In contrast, in an earlier PL investigation (Ref. 7) on doped GaN microcrystals and needle-like crystals it was shown that the properties of the 2.2 eV PL band (i.e., the temperature dependence of its intensity and half-width as well as PL excitation) can be described by a recombination model of randomly distributed shallow donors and deep acceptors—a model originally developed by Thomas and Hopfield.[8] Doping experiments gave evidence for carbon to be involved in the deep acceptor structure.

To contribute to the clarification of the situation we performed time-integrated PL experiments on state of the art undoped GaN epitaxial layers grown by metal-organic vapor phase epitaxy (MOVPE). In addition, PL decay-time measurements were performed showing a strong nonexponential decay of the PL intensity. All experiments are in line with a shallow donor to deep defect recombination to be responsible for the recombination of the 2.2 eV PL band. ODMR experiments performed on our samples show only the shallow donor related signal, which gives strong evidence that it is directly involved in the recombination process. This is further supported by the analysis of the temperature dependence of the PL intensity which gives an activation energy of about 15 meV, i.e., half of the binding energy of shallow donors in GaN, expected for uncompensated n-type material.

II. EXPERIMENTAL DETAILS

The samples used for the experiments were undoped GaN epitaxial layers grown by MOVPE on sapphire substrates. The layer thicknesses were about 3 μm. To improve the crystalline quality of the layers a 35 nm AlN buffer was grown at low temperatures. The electron concentrations of the layers as determined by C/V measurements are about 10^{17} cm^{-3} at room temperatures.

PL was excited for the steady-state experiments by the 325 nm line of a HeCd laser, and for the time-resolved measurements by a pulsed N_2 laser (3.67 eV, 300 psec pulse duration, 10 Hz repetiton rate). For its detection a photomultiplier in combination with appropriate amplifiers was used. In the time-resolved experiments the signal was fed into a storage oscilloscope or boxcar system; the overall time resolution of the system was better than 10 nsec. The sample temperature could be varied between 2 and 300 K. The ODMR experiments were performed in a 36 GHz spectrometer, where the sample was immersed in superfluid helium at 1.6 K. Details of the setups are described elsewhere.[9,10]

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III. RESULTS AND DISCUSSION

A typical low-temperature PL spectrum of the GaN samples is shown in Fig. 1. Near band gap the strong excitonic recombinaton of the donor bound excitons (D^0X) is detected. Under magnification the broad yellow band centered at about 2.2 eV becomes visible. These spectral features are typical for almost all high-quality undoped GaN samples available up to date, independently of the use of sapphire or SiC substrates.[11,12] It should be noted that the energy position and spectral shape of the yellow PL band presented here is very similar to the C-doped GaN samples used by Ogino and Aoki, and the one observed by Pankove and co-workers in their work on ion-implanted GaN.[7,13] However, in these materials the intensity of the 2.2 eV emission exceeds the exitonic recombination.

From the high-energy onset of the PL band one can already estimate that one of the recombining defects should have a deep level in the band gap of GaN. Ogino and Aoki have shown that from an analysis of the temperature dependence of the PL intensity an activation energy of about 860 meV is obtained.[7] Their investigation was performed at rather high temperatures (> 77 K). We find a second, much smaller, activation energy of 15 ± 2 meV following the PL intensity down to 5 K (inset in Fig. 1). It is approximately half of the shallow donor binding energy of 35 meV, expected for an uncompensated n-type semiconductor.[14] This observation gives already a first hint that one of the involved recombination partners is a shallow donor rather than a shallow acceptor for which the binding energies are around 230 meV.[14]

The two discussed recombination models for the yellow emission in GaN are shown in Fig. 2. Model A is the shallow donor to deep acceptor recombination model which is favored by the investigations of Ogino and Aoki. Model B was developed by Glaser and co-workers.[6] Here the yellow emission originates from a recombination between a deep double donor and a shallow acceptor. The electron transfer from the shallow donor to the deep state is assumed to occur via a spin-dependent nonradiative transfer process. Initially the shallow and deep double donor are singly occupied, and thus observable by ODMR. The yellow luminescence occurs between the neutrally charged (doubly occupied) deep donor and effective-mass acceptor states.

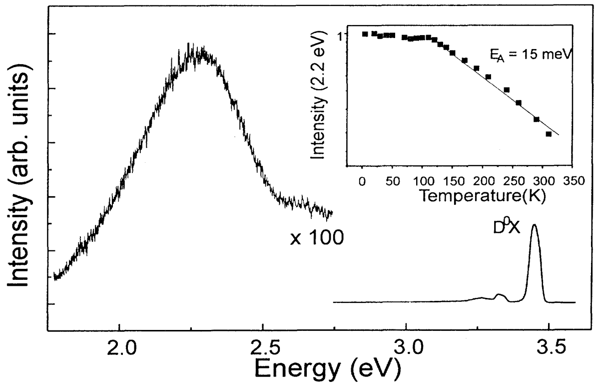

FIG. 1. Low-temperature photoluminescence spectrum of undoped GaN grown by metal-organic vapor phase epitaxy. The inset shows the intensity variation of the 2.2 eV emission as a function of temperature.

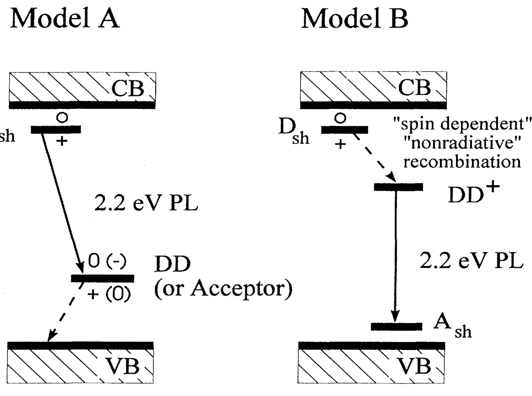

FIG. 2. Sketches of the two recombination models under the discussion for the 2.2 eV emission in GaN. Model A, shallow donor ($D_{\rm sh}$) to deep double donor (DD$^+$) or deep acceptor (A) recombination. Model B, deep donor (DD$^+$) to shallow acceptor recombination as obtained by Glaser *et al.* (Ref. 6).

To prove whether the photoluminescence excitation of the 2.2 eV band in our samples is similar to the observations of Ogino and Aoki, we describe our PLE experiments in the following, although we cannot distinguish between two models from PLE. Model B requires the deep double donor to be in a singly occupied charge state, despite the material being n-type conductive, thus the 2.2 eV PL might be excitable with light of sub-bandgap energies. According to model A one would also expect that sub-bandgap excitation is possible down to energies of onset of yellow band, i.e., about 2.5 eV, due to the possibility of direct ionization of the deep centers. Figure 3 shows the PLE spectrum obtained for the 2.2 eV

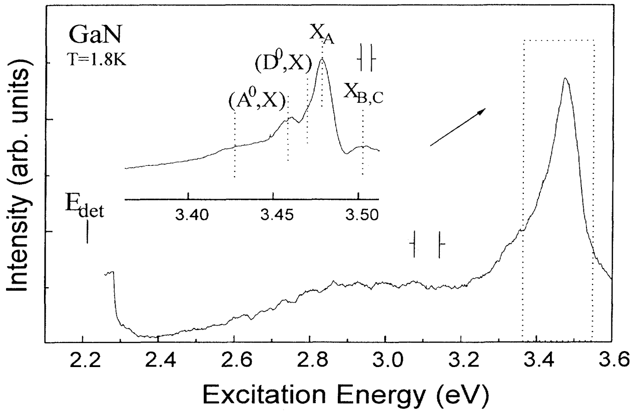

FIG. 3. Photoluminescence excitation spectrum of the 2.2 eV PL band in GaN. The inset shows the enlarged excitonic range. A^0X and D^0X denote acceptor and donor bound excitons, respectively; X_A denotes the free exciton and $X_{B,C}$ denotes the excitons of the splitoff valence band.

luminescence by using a xenon lamp in combination with a monochromator. PL excitation is possible for energies higher than 2.5 eV, very effectively with light in resonance to the excitonic transitions, in agreement with the experiments of Ogino and Aoki. In more detail, the dominant excitation line is related to the free-exciton absorption (X_A)(see the inset in Fig. 3). On the other hand, the oscillator strength of the free-exciton transition is weaker compared to that of bound exciton states.[22] This discrepancy means that overlapping of the wave functions of the excitonic states with that of the electronic states responsible for the yellow band is essential. In the PLE spectrum the absorptions due to acceptor bound excitions are more pronounced than the donor bound exciton features. Contrary, the (D^0X) line dominates in the photoluminescence spectrum, which is typical for n-type direct-band-gap semiconductors. These observations are a strong indication that the transfer of a hole from the bound exciton state to the deep state of the yellow band is involved in the excitation process. It should be noted that the equilibrium occupation of the shallow donor and acceptor states is not affected by the resonant absorption during PLE measurement due to the weak excitation level and the extremly short lifetimes of the excitonic states.[23]

Investigations of the PL decay dymanics are an appropriate tool for distingushing between models A and B. In the case of model A, a particle with an extended wave function, i.e., a shallow donor, is involved. Thus one expects to observe a broad distribution of lifetimes due to the varying separations of shallow donors and deep defects. On the other hand, for model B, where two localized particles, the deep donor and the acceptor, are involved, one expects a rather narrow lifetime distribution or even a single exponential decay time.

Figure 4 presents the experimental result of the decay-time measurement of the 2.2 eV luminescence. The decay times vary five orders of magnitude, from nanoseconds up to milliseconds. Analyzing this distribution in the Thomas and Hopfield model for distant donor-acceptor pairs we can estimate the extension of the wave function of the weakly bound particle.[8] According to this model, the intensity of emitted light at delay time t with respect to the excitation pulse is given by Eq. (1):

$$I(t) = \left\{4\pi N \int_0^\infty W(r)\exp[-W(r)t]r^2dr\right\} \times \left\{\exp\left[4\pi N \int_0^\infty \{\exp[-W(r)t] - 1\}r^2dr\right]\right\}, \quad (1)$$

where N is the concentration of the major constituent which should be of the order of the free-carrier concentration at room temperature, $W(r) = W_{\max}\exp(r/a_0)$ is the recombination probability for a single donor-acceptor pair, and a_0 is the Bohr radius of the shallow bound particle. The best fit to the data yields $a_0 = 27 \pm 3$ Å and $W_{\max} = 2.5 \times 10^7$ s^{-1}. $W_{\max}$ is of the same order as for other direct-band-gap II-VI and III-V semiconductors and a_0 is in good agreement with the Bohr radius of an effective-mass donor (28 Å, Ref. 14). Keeping all parameters constant but using an a_0 of 8 Å instead, i.e., the extension of an acceptor with $E_A \approx 230$ meV (as required by model B) does not explain the observed decay times (dashed line in Fig. 4).

So far all experiments point to a shallow donor-acceptor pair model for the recombination mechanism of the yellow band and our ODMR experiments as well do not reveal inconsistencies. We observe (Fig. 5) a single resonance with a Lorentzian line shape. Its field position is slightly dependent on the orientation of the crystal in the static magnetic field. The g value is $g = 1.95 \pm 0.01$, which is very close to the value of the effective-mass donors known from EPR experiments.[15] The resonance is increasing the PL intensity, which is usually taken as evidence that the defects are directly involved in the radiative recombination.[16,17] Compared with the observa-

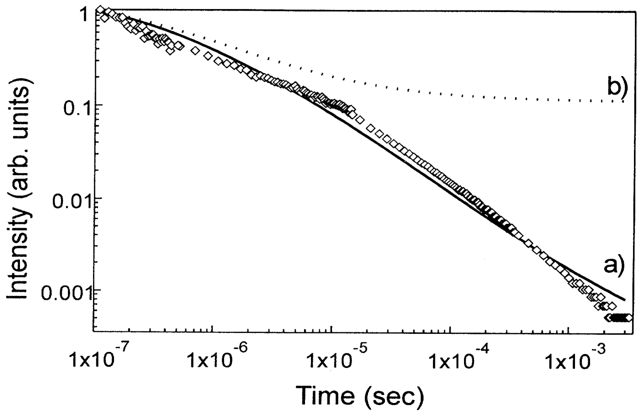

FIG. 4. Photoluminescence decay time measurement on the 2.2 eV PL band in GaN. (a) Calculated decay according to the shallow-donor–deep-donor model using a Bohr radius of 27 Å . (b) Using 8 Å ; for details see text.

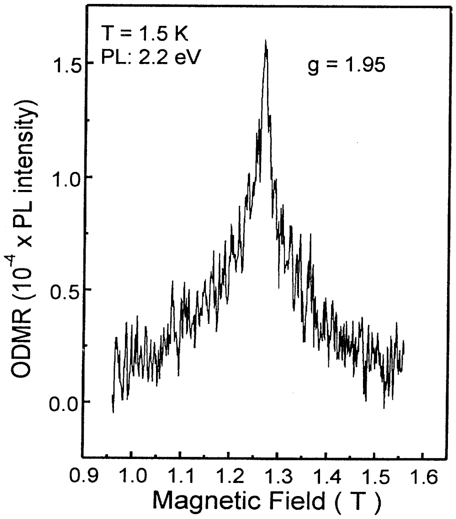

FIG. 5. Optically detected magnetic resonance spectrum observed on the 2.2 eV luminescence. The magnetic field position of the resonance correponds to a g value of 1.95, i.e., the g value of shallow donors.

tions of Glaser *et al.*, the half-width of the EMT donor resonance is rather broad (≈ 40 mT). It can be explained by the higher donor concentration of our samples which, due to exchange interaction, leads to the broadening of the signal.[16] The shallow donor ODMR signal is also observable in the yellow luminescence changing the PL excitation conditions to sub-bandgap conditions, i.e., using the 442 nm (2.8 eV) line of the HeCd laser instead of the 325 nm line. In model *B* the excitation channel of lowest energy involving the shallow donor level is to directly ionize a shallow acceptor and to transfer the electron to the conduction band. It requires photon energies > 3.2 eV. Excitation of the 2.2 eV PL with 2.8 eV photons and the observation of the shallow donor resonance enhancing the PL intensity under this condition further supports model *A*. The deep donor signal reported by Glaser *et al.* (labeled *A*1) should appear on the low field side of the EMT donor. Unfortunately, the large linewidth of the shallow donor signal prevents its observation.

To associate the *A*1 resonance with a deep acceptor, according to model *A*, is in conflict with the observed g values ($g_{\|} = 1.989, g_{\perp} = 1.992$) which are slightly smaller than the free-electron value of $g_e = 2.0023$. In first-order perturbation theory the deviation of the g value is given by $g \approx \lambda/\Delta E$; λ is the spin-orbit interaction constant.[18] Thus, electron centers (negative λ) should show g values smaller than the free-electron value and hole centers should have a positive g shift. Exceptions to this rule are known. For example, arsenic antisite defects in GaAs which are double donors have a g value of 2.04.[19] However, the negative g shift is a strong argument for the observation of a donor-type defect.

In the case of a shallow-donor–deep-acceptor recombination we would expect to find an energy dispersion in the PL band, in addition to the lifetime dispersion. It is due to the Coulombic interaction between donors and acceptors. The emission energy ($h\nu$) of a donor - acceptor pair with separation r is given by[7]

$$h\nu = E_{\mathrm{gap}} - E_D - E_A + e^2/\epsilon r. \tag{2}$$

Pairs with a small separation are expected to emit on the high-energy side of the PL band with a short lifetime. Pairs with a large separation should preferentially be found on the low-energy side of the PL band having long lifetimes. The expected energy difference can be calculated from the shallow donor concentration.[20] It should be between 5 and 10 meV for the samples used in our experiments. Figure 6 shows three time-delayed PL spectra of the yellow band, setting delay-time and gate-width of the boxcar system as indicated. An energy shift of the yellow band is not observed. The broadening on the high-energy side is caused by another PL band which becomes only observable under the high excitation conditions. This PL band has a fast decay time and its emission maximum is at 2.95 eV. More details concerning this band will be reported elsewhere.[21] These experiments give evidence that there is almost no, or only a very small, Coulombic interaction between the two recombination partners of the 2.2 eV band, i.e., it is more likely to be of shallow-donor–deep-donor type.

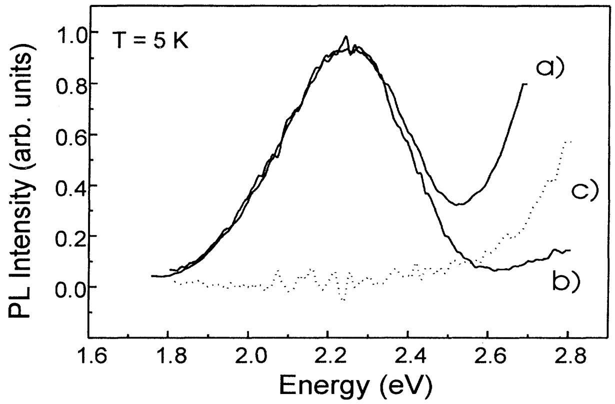

FIG. 6. Time-delayed photoluminescence spectra of the 2.2 eV band in GaN: (a) using a delay time 0.1 μs and a gate width of 1 μs; (b) with delay and gate settings of both 500 μs; and (c) numerical substraction of (a) and (b), showing that the energetical shift of the 2.2 eV band is caused by the second PL band on the high-energy side of the spectra.

This model can also consistently explain the observation of the deep donor (DD) ODMR and in the n-type material, if the deep donor is a double donor (as already proposed by Glaser *et al.*[6]):

$$D^+ + DD^0 + h\nu(\mathrm{exc}) \rightarrow D^0 + DD^+ + h\nu(2.2\ \mathrm{eV}). \tag{3}$$

Before excitation the deep double donor is neutral. After excitation a hole is trapped at the deep double donor creating its singly occupied (paramagnetic) charge state. Both shallow and deep donors are directly involved in the 2.2 eV recombination and thus the ODMR signals are observed as an increase of the PL intensity.

Our experiments do not tell anything about the nature of the deep center, but the presence of the 2.2 eV PL in almost all kinds of GaN samples independent of the growth techniques indicates it to be of intrinsic origin. The nitrogen vacancy as suggested earlier (Ref. 5) as well as the Gallium interstitial are intrinsic donors in GaN and might be candidates. Furthermore, on the basis of spatially resolved measurements we have found that the yellow luminescence intensity is much higher in the close neighborhood of the interface to the substrate. This also indicates that native defects are involved.

In conclusion, our experiments strongly support a shallow-donor–deep-donor model for the recombination mechanism of the yellow (2.2 eV) PL in GaN. This model also allows us to explain consistently the observation of the corresponding ODMR signals in n-type GaN.

ACKNOWLEDGMENTS

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