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DYNAMICAL STUDY OF THE YELLOW LUMINESCENCE BAND IN GaN

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Abstract—A comprehensive study of the yellow photoluminescence (YL) in GaN epitaxial films grown by hydrid vapor phase epitaxy and by metal organic vapor phase epitaxy is presented including time-integrated and time-resolved photoluminescence (PL), PL excitation (PLE) and optically detected magnetic resonance (ODMR) experiments. ODMR reveals the participation of shallow and deep double donors based on the analysis of the g-values. This recombination model is supported by time-resolved investigations. PLE spectra show a close connection between the excitation processes of the YL band and of the inner transition of Fe^{3+} at 1.293 eV. Two-color stimulation experiments prove energy transfer between YL and the Fe^{3+} center by hole transfer, strongly confirming the YL recombination model involving a deep level 1.2 eV above the valence band. © 1997 Elsevier Science Ltd

1. INTRODUCTION

In recent years the development of an AlGaN/InGaN light emitting diode (LED)[1] stimulated worldwide efforts to develop a blue laser. The electroluminescence of the above mentioned LEDs at room temperature shows unambiguously that impurities are involved in the luminescence process. Since almost all GaN epitaxial films independent of the growth technique show the yellow photoluminescence band (YL) around 2.2 eV it is important to understand the recombination mechanism and the defects involved. In recent investigations the signals observed by optically detected magnetic resonance (ODMR) on the 2.2 eV photoluminescence (PL) in undoped epitaxial layers were attributed to an intrinsic defect[2–4]. 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[4]. In contrast, in earlier PL investigations[5] on doped GaN microcrystals and needle-like crystals it was shown that the YL band can be described by a recombination model of randomly distributed shallow donors and deep acceptors. Doping experiments indicated that carbon is involved in the deep acceptor structure.

The purpose of this paper is to clarify the recombination model for the yellow luminescence by performing time-integrated and time-resolved PL investigations. Additionally, PL excitation (PLE) and two-color stimulation experiments yield information about the energy positions of the impurities involved in the forbidden gap of GaN.

2. SAMPLES AND EXPERIMENTAL

The investigated bulk-like sample with a thickness of 400 μm was grown by hydride vapor phase epitaxy without any buffer layer. The metal organic vapor phase epitaxy epilayers of thickness around 3 μm were deposited on a 35 μm AlN buffer. All samples investigated here were grown on sapphire substrates. The electron concentrations of the layers determined by CV measurements were around 10^{17} cm^{-3} at room temperature.

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. The PLE measurements and the two-color stimulation experiments were performed with either a monochromator/tungsten lamp combination as tunable light source or a semiconductor laser providing 50 mW at 830 nm. The ODMR investigations were performed in a 36 GHz spectrometer with the sample immersed in superfluid He at 1.6 K.

3. EXPERIMENTAL RESULTS

A typical low-temperature PL spectrum of the GaN samples is shown in Fig. 1. Near the bandgap (upper spectrum) the strong excitonic recombination

of the donor-bound exciton (D_0,X), a weak donor–acceptor-pair (DAP) luminescence and a broad yellow band are detected. It should be noticed that the luminescence intensity of YL increases strongly if the sample is excited from the sapphire side. This indicates that the luminescence of YL comes mainly from the near interface area. This is in agreement with spatially resolved experiments where we could demonstrate that the YL band stems mainly from a region several micrometers thick at the interface[6]. From the analysis of the temperature dependence of the PL intensity an activation energy of (15 ± 2) meV is determined (inset of Fig. 2), which is approximately half the shallow donor binding energy of 35 meV[7]. This behavior is expected for an uncompensated n-type semiconductor if one of the recombination partners involved in the YL band is the intrinsic shallow donor.

Nearly all GaN samples investigated show a series of luminescence lines in the near infrared spectral region (see lower part of Fig. 1), which recently could be attributed to inner transitions of Fe^{3+}, Ti^{2+}, and V^{3+}[8–11].

To clarify the recombination model of the YL band we performed comparative PLE of YL and of the Fe^{3+} luminescence (shown in Fig. 2). In general we observe a very similar excitation behavior for both PL transitions indicating a close connection of the excitation processes. The dominant excitation line

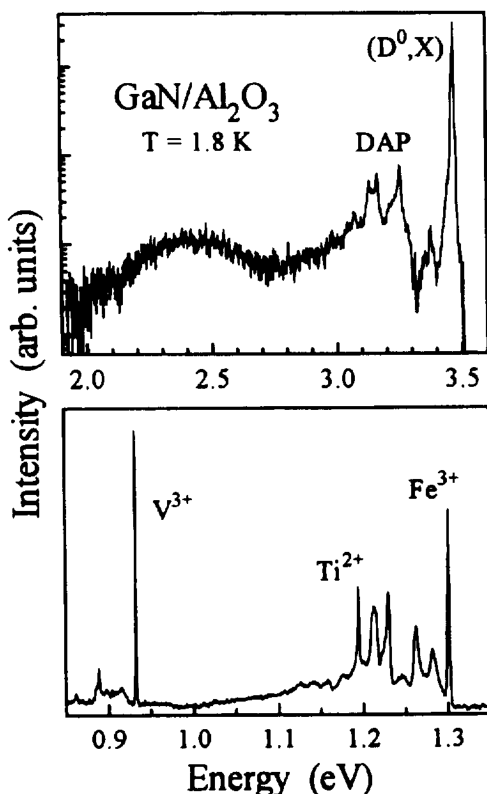

Fig. 1. Low temperature PL spectra of undoped GaN grown by hydride vapor phase epitaxy.

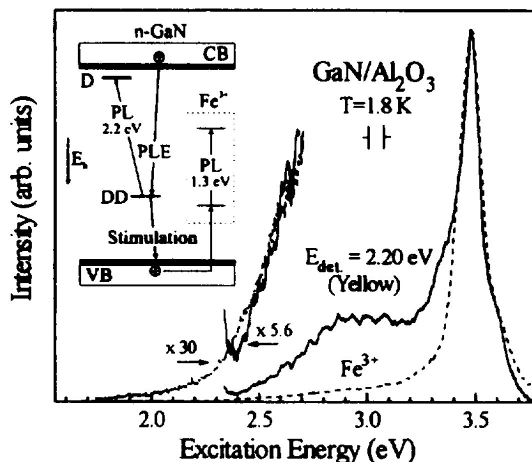

Fig. 2. PLE spectra of the YL and of the Fe^{3+} luminescence. The inset shows the term scheme of the YL and Fe^{3+} recombination and excitation processes. The observed transitions are given as hole transitions to account for the n-type character of the samples.

around 3.5 eV is related to free- and bound-exciton absorption. Obviously, capture of free carriers and energy transfer processes from bound-exciton complexes represent the most efficient excitation channel. The onset at 2.3 eV in PLE spectrum of the 2.2 eV luminescence in the n-type samples implies a direct excitation process (see term scheme in the inset of Fig. 2) and demonstrates that a deep impurity level around 2.3 eV below the bottom of the conduction band is involved with the YL band. Excitation of the Fe^{3+} PL in the n-type samples needs the generation and subsequent capture of holes in the valence band. These processes result in the high excitation efficiency in the near bandgap region. However, the Fe^{3+} PLE spectrum reveals also well below the bandgap excitation having the same low energy onset as observed for the YL band but much weaker. This observation indicates two-step generation of free holes in the valence band via the deep level of the YL band.

To prove this model we performed two-color stimulation spectroscopy (Fig. 3). The intensity of the YL band excited by UV excitation is found to quench by additional illumination in the near infrared spectral region. An excitation spectrum of the quenching of the YL band (Fig. 3) shows a low energy threshold at 1.2 eV, corresponding well to the position of the deep defect of the YL. Employing 50 mW at 1.50 eV for the stimulation the YL quenches by 16%. Simultaneously, the inner Fe^{3+} transition is stimulated by 9% (inset of Fig. 3). The 1.50 eV excitation alone does not excite the Fe^{3+} PL. This indicates unambiguously, that holes from the deep defect involved in the YL recombination are transferred to the Fe center generating excited Fe^{3+} centers under the impact of the additional irradiation in the near infrared spectral range (see the term scheme in the inset of Fig. 2). Excitation of Fe^{3+} PL

by hole transfer processes is well known for the wide bandgap II–VI semiconductors[12].

Time-resolved measurements of the YL band reveal a non-exponential decay over six orders of magnitude which is typical for a DAP recombination. Fitting the decay curve with the model of Thomas and Hopfield[13,14] we got a Bohr radius $a_0 = (2.7 \pm 0.3)$ nm and net donor concentration of 3×10^{17} cm^{-3}. This indicates that effective mass donors are directly involved in the recombination process of the YL band. Time-delayed PL spectra show no shift of the maximum of the YL band indicating that the recombination is of a shallow donor/deep donor type.

A typical ODMR spectrum for the YL band is shown in Fig. 4. Two resonances with g-values of 1.95 ± 0.01 and 1.98 ± 0.01 were observed. The g-value of 1.95 is very close to the g-value of the effective mass donor known from EPR[15] and of the g-value derived from Zeeman results of the donor-bound exciton (D_0,X)[16]. The 1.98 g-value agrees with the deep-donor signal reported by Glaser *et al.*[4].

4. DISCUSSION

Two mechanisms of the YL band have been proposed in the literature. The first one is a transition from a shallow donor state to a deep localized state[5], while the second mechanism[4] describes a transition from a deep double donor to a shallow acceptor state. Perlin *et al.*[17] found a freeze-out of electrons in n-type GaN for hydrostatic pressures above 20 GPa. This effect is explained as an emergence of a conduction band resonance acting as shallow donor into the forbidden gap. The pressure dependence of the YL is very similar to that of the n-conductivity, which suggests the YL to be due to transitions between shallow donors and deep acceptors[17]. Our present results for the YL in n-type GaN give clear evidence that the excited state is a shallow donor. Additionally, the ODMR and the time-resolved PL results show that the final state is a deep double donor. Therefore, we propose as a mechanism for the YL band a transition from a shallow donor to a deep double donor state. Furthermore, our spatially resolved investigations show that the YL stems mainly from a thin region at the GaN/substrate interface indicating that the deep double donor state is probably a complex where deep point defects are bound to dislocations.

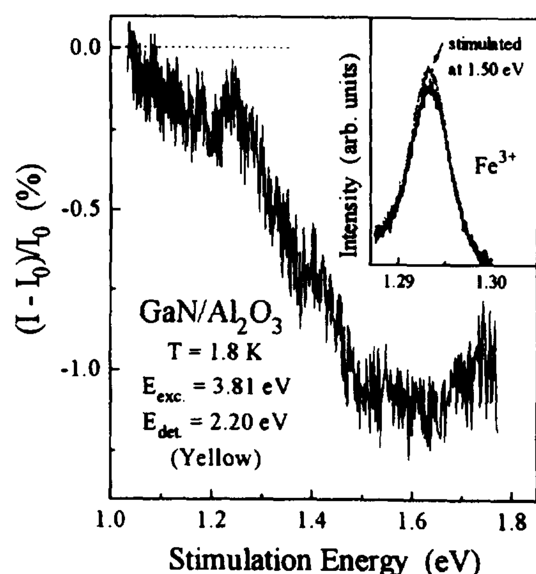

Fig. 3. Stimulation spectrum of the YL, exciting with a HeCd laser and a tunable near infrared light source. The inset shows the stimulation of the Fe^{3+} luminescence by 50 mW, 1.50 eV secondary illumination.

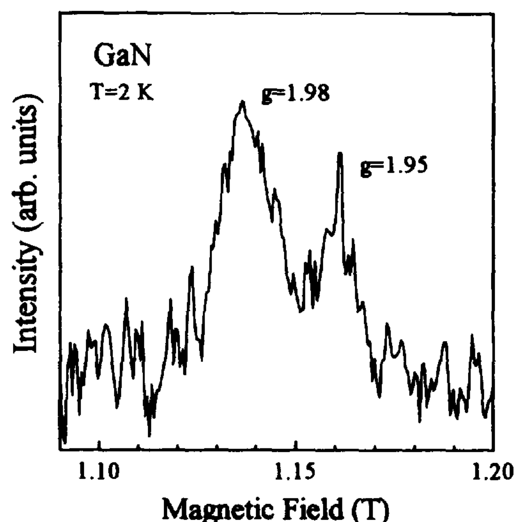

Fig. 4. ODMR spectrum of the 2.2 eV luminescence.

The recombination and excitation processes observed in this work are summarized in the term scheme given as the inset in Fig. 2. The transitions are given as hole transitions to account for the n-type character of the samples. The sum of the low energy thresholds of the YL PLE and the YL stimulation at 2.3 and 1.2 eV, respectively, give together the bandgap energy and locate the deep double donor 1.2 eV above the valence band. The two-color stimulation results show that the quenching of the YL and the stimulation of the inner Fe^{3+} luminescence results from energy transfer processes via free holes in the valence band.

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