

Impact of the ZnO buffer on the optical properties of GaN: time resolved micro-photoluminescence

A. Hoffmann ^{a,*}, J. Holst ^a, A. Kaschner ^a, H. Siegle ^a, J. Christen ^b, P. Fischer ^b,
F. Bertram ^b, K. Hiramatsu ^c

^a *Institut für Festkörperphysik, TU Berlin, Hardenbergstraße 36, 10623 Berlin, Germany*

^b *Institut für Experimentelle Physik, Otto-von-Guericke-Universität, Universitätsplatz 2, 39016 Magdeburg, Germany*

^c *Department of Electrical and Electronic Engineering, Mie University, Mie 514-8507, Japan*

Abstract

Spatially-resolved and time-resolved micro-photoluminescence (μ -PL) investigations were performed on thick GaN layers. Our measurements reveal that the peak position of the excitonic transition lines strongly depends on the distance to the substrate interface. The luminescence is shifted continuously to lower energies with decreasing distance, however, a strong blue shift occurs directly at the interface. The sample exhibits morphologically separated channels emitting at different energies and having different temporal behaviors. These different channels could be explained by the incorporation of O and Zn impurities, since ZnO buffer layers were used and disappeared after growing GaN on the substrate/buffer layer. Time-resolved luminescence investigations demonstrate that there is a strong energy transfer between the Zn and O channels. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The major problem for epitaxial growth of GaN is the lack of lattice matched as well as thermal expansion matched substrate material. AlN, and in some cases ZnO, are often used to reduce the strain in the active layer. Introducing ZnO buffer layer significantly improves the optical properties of GaN epilayers. However, the precise role of ZnO buffer and interface to the GaN as well as the possible decomposition during growth has not received much attention so far. Recently [1], we demonstrated that Zn and O are incorporated in the GaN if ZnO is used as buffer layer. From cathodoluminescence (CL) investigations on a 220- μ m-thick GaN layer grown by hydrogen vapor phase epitaxy (HVPE), it was possible to make visible the strongly inhomogeneous, columnar-like structure of the GaN. Locally separated morphological channels running parallel throughout the 220 μ m thickness are

clearly seen (Fig. 1). Parallel to the c -axis, we observe a light gray stripe pattern where the wavelength of the luminescence light is ~ 360 nm, while between these pattern (plotted in dark gray) the integral spectrum is blue shifted. These different channels have been attributed to Zn and O incorporation by [1]. Therefore, the purpose of this paper is to study the spatially varying, i.e. thickness-dependent influence of strain and defects on the optical properties in heteroepitaxial GaN using time- and spatially-resolved micro-photoluminescence (μ -PL) experiments. This technique allowed us to map the vertical luminescence distribution in the layer, thus extracting the dependence of the optical properties on the layer thickness. In contrast to an investigation on a series of samples with varying thickness, spatially-resolved measurements avoid possible mistakes caused by comparing different samples grown and treated under slightly different conditions. In order to obtain information about energy transfer processes between the two different impurity channels we carried out time-resolved experiments of the same region investigated by μ -PL measurements with a comparable spatial resolution.

* Corresponding author.

E-mail address: hoffmann@physik.tu-berlin.de (A. Hoffmann)

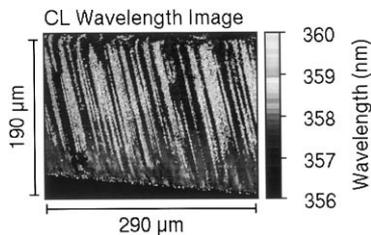


Fig. 1. Cathodoluminescence wavelength image of the investigated sample. Channels with different dominant recombination processes are to be seen.

2. Experimental setup

The sample under study was an undoped 220 μm thick hexagonal GaN layer grown on (0001) sapphire using hydride vapor phase epitaxy (HVPE) with a ZnO buffer layer. Details of the growth method can be found in [2].

The scanning $\mu\text{-PL}$ is based on a modified microscope (Zeiss MPM 400/800) combined with a continuous He cryostat (4–325 K). A high resolution piezo stage enables scanning with a lateral step resolution of 1 nm. In addition, for large scanning distances, we used a DC-monitor driven scanning stage with a resolution of 250 nm allowing us to investigate areas larger than 10×10 mm. As an excitation source for time-resolved $\mu\text{-PL}$, we used a frequency-doubled dye laser synchronously pumped by an actively mode-locked and frequency-doubled Nd:YAG laser. The overall time resolution of this system is 15 ps by convolution techniques. An overall spatial resolution of $\Delta x < 600$ nm is obtained under optimum conditions. The complete $\mu\text{-PL}$ spectrum is recorded at each pixel (x,y) during scanning over 128×100 pixels. After image scanning is completed, a 3D data set $I(x,y,z)$ is obtained and all types of data cross sections through this tensor can be

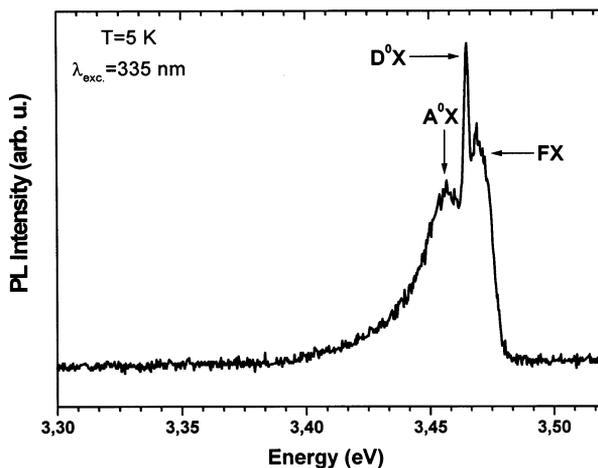


Fig. 2. $\mu\text{-PL}$ spectrum of the GaN layer 50 μm away from the interface in one of the dark gray channels of Fig. 1.

generated. Typical examples of such extracted information are locally time-resolved and -integrated PL spot spectra $I(\lambda, x_i, y_i)$, PL wavelength images, i.e. mapping of local emission peak wavelength $\lambda_{\text{Peak}}(x,y)$, sets of monochromatic PL images $I(\lambda_i, x, y)$ as well as PL spectrum linescans $I(\lambda_i, S(x,y))$.

3. Results

A low-temperature photoluminescence spectra of thick GaN epilayers grown by HVPE show near the surface (50 μm away from the substrate interface in the dark gray channel of Fig. 1) the free-exciton emission ($FX(A)$) at 3.471 eV, the neutral-donor-bound-exciton (D^0, X) emission line I_2 at 3.465 eV and a weak emission line I_1 at 3.455 eV which can be attributed to the annihilation of excitons bound to neutral shallow acceptors (A^0, X) (Fig. 2). In high quality samples, the low-energy side of the excitonic spectrum is dominated by their phonon sidebands. Our micro-PL measurements described in [3] reveal that the energy positions of the excitonic luminescence change drastically when moving the exciting laser spot nearer to the substrate interface. According to the different luminescence shifts, one can divide the layer into four regions. In the first region, for distances in the range 220–170 μm , no shift could be observed, i.e. all spectra are quite similar. In the second region for distances $170 < d < 30$ μm , the I_2 as well as the free-exciton emission shift by ~ 6 meV. This red shift is compensated by the following blue shift in the third region ($30 < d < 2$ μm). In the fourth region, a peak on the high-energy side of the free-exciton emission line becomes dominating. To get a deeper understanding of the observed red and blue shifts of the excitonic PL, a $\mu\text{-PL}$ linescan along the dark gray channels of Fig. 1 showed that two different types of blue shifts occur near to the substrate interface. The first shifts the excitonic luminescence to higher energies and compensates the former red shift. The second is an additional luminescence process. For distances $d < 10$ μm , a shoulder appears above the free-exciton emission line which increases in intensity for decreasing distance to the substrate. For distances below 2.0 μm , this structure peaking at ~ 3.49 eV becomes the dominant luminescence process.

A $\mu\text{-PL}$ linescan along the light channels of Fig. 1 showed a relatively broad luminescence band near the spectral position of the acceptor bound exciton. This excitonic band remains almost constant in energy between the surface and until 80 μm from the interface and then weakly shifts to blue photon energies. A blue shifted luminescence band at 3.49 eV occurs mainly near the interface.

In order to understand the spatial dependency of the luminescence, we performed micro-Raman scattering

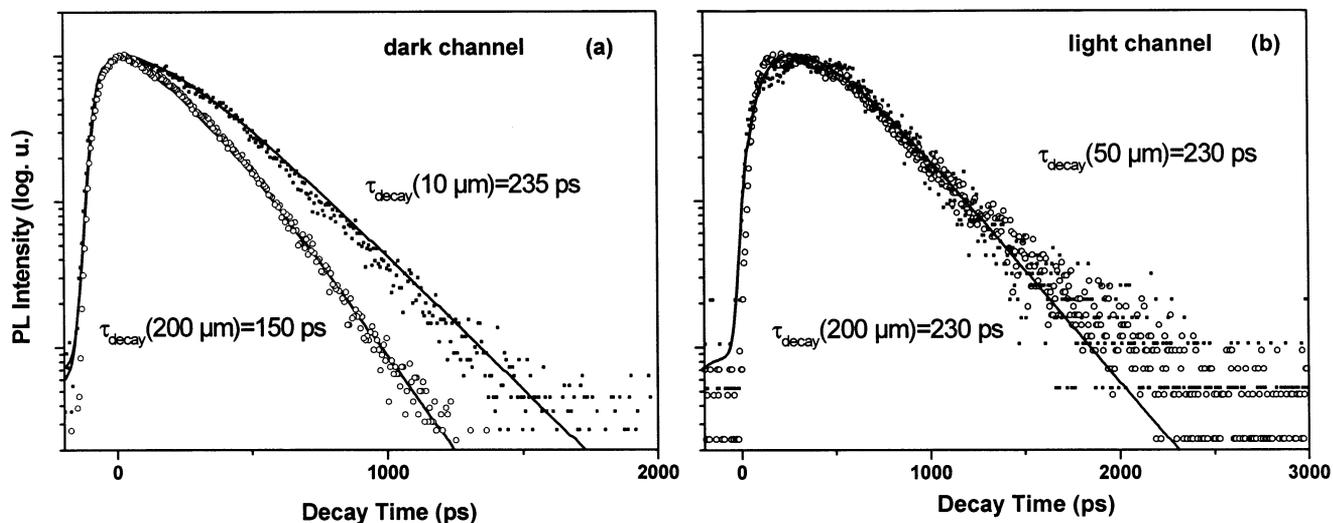


Fig. 3. Monoexponential decay of the μ -PL at two different detection channels: (a) dark channels at 357 nm show a change of with the distance from the substrate; (b) the decay of the light channels at 359 nm does not vary.

experiments on the same region where we took the CL linescans. All Raman measurements were carried out at 4.2 K to ensure comparable conditions. By measuring the shift of the E_2 Raman mode of the GaN layer, we were able to determine the strain in our sample as a function of the distance to the substrate. We found that the stress in the GaN layer almost decreases exponentially with an increasing distance to the substrate. The layer is already relaxed to a large extent at a distance $d = 30 \mu\text{m}$ away from the substrate. For distances $d > 100 \mu\text{m}$, the layer is fully relaxed.

Unpolarized low-temperature micro-Raman spectra taken at various distances to the substrate interface in $\chi(\cdot)\chi$ scattering geometry show that near the surface of the layer, only the expected GaN Raman modes peaking at ~ 533 ($A_1(TO)$), 560 ($E_1(TO)$), 567 (E_2) and 742 cm^{-1} ($E_1(LO)$) are present in the spectra per micrometer, respectively [4]. At a distance of 170 μm (50 μm below the surface), a broader structure below the $A_1(TO)$, i.e. the LPP^- mode, becomes visible. This mode shifts continuously to a higher frequency with a decreasing distance to the substrate. Simultaneously, a plasma mode structure LPP^- at $\sim 650 \text{cm}^{-1}$ known from highly doped GaN [5,6] appears and becomes stronger for a decreasing distance while the $E_1(LO)$ decreases in intensity. This observation indicates that the free-carrier concentration in the thick GaN layer increases gradually with a decreasing distance to the substrate. From the energy position of the LPP^- mode, we were able to estimate the free-carrier concentration according to the procedure described in [5]. We found that the free-carrier concentration increases from $\sim 8 \times 10^{17} \text{cm}^{-3}$ near the surface of the GaN layer to $1 \times 10^{20} \text{cm}^{-3}$ at the substrate interface. Thus, apart from the strain gradient, there is also a gradient of the

free-carrier concentration in the GaN layer. There are two reasons for the observed doping gradient. On one hand, the defect density due to the unfavorable growth conditions decreases strongly with increasing layer thickness. On the other hand, the concentration of atoms diffused from the buffer layer and from the substrate into the layer during growth also decreases with increasing distance to the substrate. While the high free-carrier density directly at the substrate mainly results from the first effect, several groups reported the formation of amorphous mediate layers at the substrate interface. We believe that the high doping level found 55 μm away from the substrate interface could be explained by indiffusion of Zn or O impurities because of the ZnO buffer layer which disappeared after growing GaN on the substrate/buffer layer.

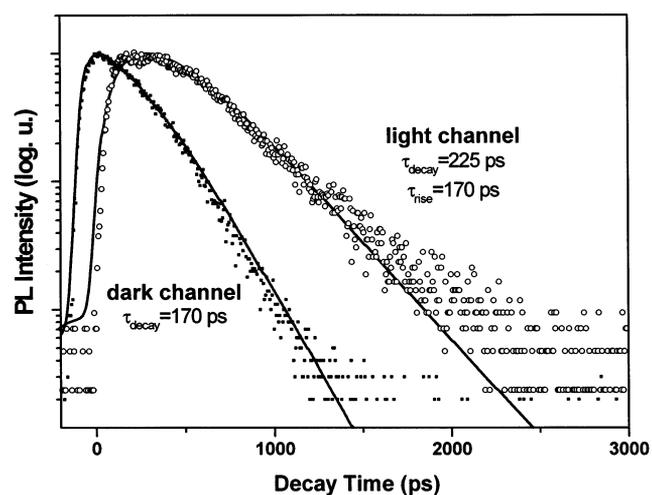


Fig. 4. Temporal behavior of the μ -PL at two different spots. For the light channels the onset of the decay can be explained by a carrier transfer.

Table 1
Time-resolved μ -PL^a

λ (nm)	Distance from interface (μm)	τ_{rise} (ps)	τ_{decay} (ps)
357 nm 'dark channel'	2	195	
	10		235
	50		200
	150		170
	200		150
359 nm 'light channel'	50	200	220
	100	180	230
	150	170	225

^a Decay- and rise-times of the different excitonic transitions at two different detection channels are summarized.

While the optical and structural properties of the first region of the GaN layer do not change markedly with the distance to the substrate, the red shift occurring in the second region indicates a reduction of the bandgap of the GaN layer. Since this red shift can be observed for bound as well as free-exciton emission, a different recombination channel gradually opening with decreasing distance to the substrate, e.g. a deeper-bound exciton, can be ruled out; the binding energy remains constant over the distance. Tensile strain can also be excluded because a stress-induced shift of the excitonic PL should be accompanied by a softening of the E_2 Raman mode. Biaxial stress of one GPa shifts the near-band-edge PL lines by 27 meV and the E_2 Raman mode by 4.2 cm^{-1} [7]. From this, one expects a softening of the E_2 mode of $\sim 0.9 \text{ cm}^{-1}$, which we did not observe in our micro-Raman measurements. In contrast, we found a biaxial compressive strain which reduces exponentially with decreasing distance. In the region where the red shift takes place, most of the strain is already relaxed (only near the surface is the GaN sample compressively strained). To get a better understanding of the observed red shift of the excitonic luminescence, we have performed time-resolved measurements of the excitonic luminescence as a function of the distance to the interface in the two morphologically separated channels. In the dark gray channels, the decay time of the excitonic luminescence strongly depends on the distance to the interface. In the first 40 μm from the interface to the surface, the decay time increases. This could be understood from the decrease in the free carrier concentration determined by the above mentioned Raman investigations (Fig. 3). After 50 μm from the interface, we observe a pattern of dark and light gray channels (Fig. 1). In the light gray channels, the decay time of the excitonic luminescence remains constant (Fig. 4), however, we have a different rise time dependent on the distance to the surface of the GaN layer. These rise times as a function of the distance to

the surface fit well with the decay times of the excitonic luminescence in the dark channels. Here, no rise time can be observed. Therefore, we assume that an energy transfer from the dark gray into the light gray channels occurs, resulting in a faster decay of the excitonic luminescence in the dark gray channels. In Table 1, all observed rise and decay times for the different morphological channels are summarized. We believe that Zn and O are incorporated in the light gray- and dark channels, respectively. The observed red shift in the dark channels may be explained by an interaction between neighboring channels through an piezo-electric field induced by the in-built Zn.

In the third region, the red shift of the excitonic luminescence turns into a blue shift. This compensates the former red shift and can simply be explained by the increasing compressive strain with decreasing distance to the substrate. The hardening of the E_2 mode found in our micro-Raman measurements is 0.8 cm^{-1} which corresponds to a change of the excitonic energy position of 5.2 meV following the relation given in [7]. This value agrees very well with our results.

Apart from the blue shift of the excitonic luminescence an additional band appears in the fourth region directly at the substrate interface. We attribute this structure which peaks above the bandgap energy of the GaN layer to band-to-band transitions. Our Raman experiments show that the free-carrier concentration in this region is $\sim 1 \times 10^{20} \text{ cm}^{-3}$. Therefore, the doping density reaches a level at which band-to-band transitions can occur even at low temperatures. This blue shift as a function of an increasing free carrier concentration is typical for band–band transitions if the Fermi-level crosses the conduction band (band filling) [8]. Our assignment also agrees with the observations of Cunningham et al. [9] who performed PL measurements on a series of samples with varying doping levels. Eckey et al. [10] also observed this blue shift in their PL measurements where the carrier concentration was induced by high excitation.

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