

# Spatially resolved investigations of the excitonic luminescence in GaN

A. Hoffmann <sup>a,\*</sup>, J. Christen <sup>b</sup>, H. Siegle <sup>a</sup>, F. Bertram <sup>b</sup>, D. Schmidt <sup>b</sup>, L. Eckey <sup>a</sup>,  
C. Thomsen <sup>a</sup>, K. Hiramatsu <sup>c</sup>

<sup>a</sup> *Institut für Festkörperphysik, TU Berlin, Hardenbergstraße 36, 10623 Berlin, Germany*

<sup>b</sup> *Institut für Experimentelle Physik, Otto-von-Guericke-Universität, Universitätsplatz 2, 39016 Magdeburg, Germany*

<sup>c</sup> *Department of Electrical and Electronic Engineering, Mie University, Mie 514-8507, Japan*

## Abstract

We performed spatially-resolved investigations on thick GaN layers using cathodoluminescence and micro-Raman experiments. 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. We correlate these effects with bandgap renormalization and band filling effects induced by a strong gradient of free-carrier concentration in addition to a strain gradient found by our Raman experiments. © 1997 Elsevier Science S.A.

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## 1. Introduction

With the development of the first multilayer nitride laser structure [1], the job to understand and to quantify the residual strain becomes more urgent. GaN layers and also their substrates are highly strained through the large mismatch of lattice constants and thermal expansion coefficients between layer and common substrates. The unfavorable growth conditions results in high defect concentrations in the layers which are not homogeneously distributed [2,3]. 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 spatially-resolved cathodoluminescence (CL) 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 independent information about strain and doping distribution in the layer, we carried out micro-Raman scattering experiments of the same region investigated by CL measurements with a comparable spatial resolution.

## 2. Experimental setup

The sample under study was an undoped 220  $\mu\text{m}$  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 [4].

The low-temperature (1.8 K) cathodoluminescence measurements were performed in a fully computer-controlled modified scanning microscope (SEM). In the mode CL wavelength imaging (CLWI), the electron beam is digitally scanned over a rectangular area (in Fig. 1, e.g.  $190 \times 290 \mu\text{m}^2$ ). The best spectral resolution is better than 100 nm. Details and applications of this technique are given elsewhere [5].

Micro-Raman measurements were carried out with a triple-grating Dilor spectrometer and the 515.4 nm line of an  $\text{Ar}^+$  laser for excitation. The spatial resolution

\* Corresponding author. Fax: +49 30 31422064; e-mail: axel0431@mailszrz.zrz.tu-berlin.de

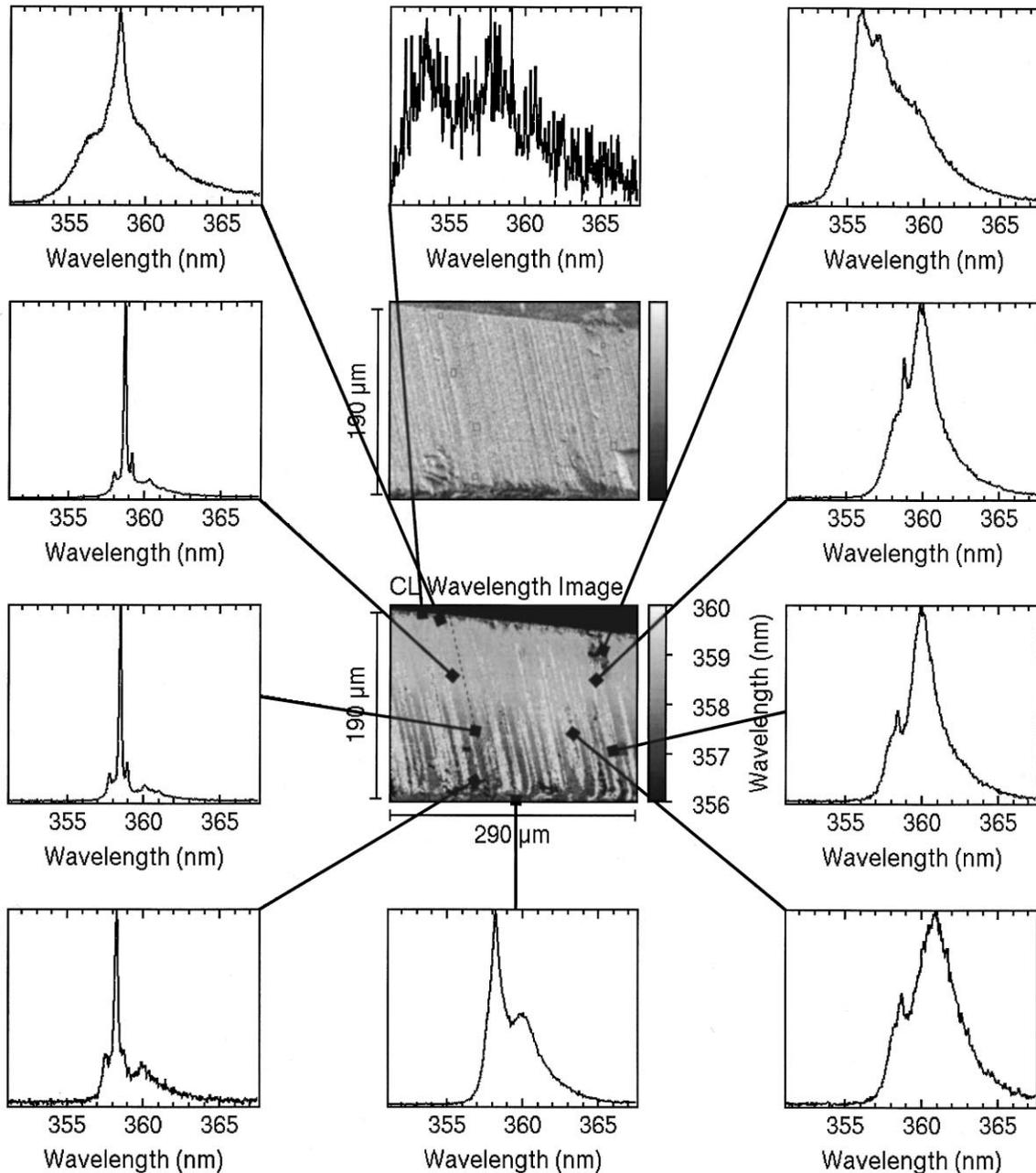


Fig. 1. Local spot mode CL spectra at different positions of a thick GaN sample. In the center, the scanning microscope and CL wavelength images are to be seen.

was better than  $1 \mu\text{m}$ . We were able to detect Raman shifts smaller than  $0.1 \text{ cm}^{-1}$ .

### 3. Results

Typical low-temperature photoluminescence spectra of thick GaN epilayers grown by HVPE show near the surface (far away from the substrate interface, where we have bulk condition) the free-exciton emission (FX(A)) at  $356.5 \text{ nm}$  ( $3.478 \text{ eV}$ ), the neutral-donor-bound-exci-

ton ( $D^0, X$ ) emission line  $I_2$  at  $357.1 \text{ nm}$  ( $3.472 \text{ eV}$ ) and a weak emission line  $I_1$  at  $359.4 \text{ nm}$  ( $3.450 \text{ eV}$ ) which can be attributed to the annihilation of excitons bound to neutral shallow acceptors ( $A^0, X$ ) (see for example, the lowest spectrum of Fig. 1 on the left hand side and [6]). In high-quality samples, the low-energy side of the excitonic spectrum is dominated by their phonon sidebands. The strength of the second LO replica of the free excitons is stronger than that of the donor-acceptor-pair luminescence [6]. This statement is supported by the small half-widths of the exciton lines ( $< 1 \text{ meV}$ ).

Our micro-photoluminescence (PL) measurements described in [7] reveal that the energy positions of the excitonic luminescence change drastically when moving the exciting laser spot nearer to the substrate interface. To get a deeper understanding of the observed red and blue shifts of the excitonic PL, Fig. 1 represents highly resolved CL spectra with a spectral resolution better than 100 nm. In the center of Fig. 1, the CL wavelength image is shown. Parallel to the *c*-axis we observe a light gray stripe pattern, where the wavelength of the luminescence light is around 360 nm, while between these patterns (plotted in dark gray) the integral spectrum is blue shifted. Typical local spot CL spectra of the stripe pattern can be seen on the right hand side of Fig. 1, on the left hand side, CL spectra of the blue range are plotted, while on the top and bottom, luminescence spectra from the interface and the surface are represented, respectively. Considering the linescan along the dark channel shown in Fig. 2(b), the red shift of the  $I_2$  clearly follows the free-exciton emission. Consequently, a different excitonic recombination process, e.g. excitons bound to a different donor, can be ruled out as an explanation for the red shift.

From the CL linescan near the interface in Fig. 2(b), it becomes clear 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  $d < 10 \mu\text{m}$ , a shoulder appears above the free-exciton emission line which increases in intensity with decreasing distance to the substrate. For distances below 2.0  $\mu\text{m}$ , this structure, peaking at about 3.515 eV (352.7 nm) (see also Fig. 1, the top local plot spectrum in the middle), becomes the dominant luminescence process.

Fig. 2(c) exhibits the CL linescan along the light channel where a relatively broad luminescence band near the spectral position of the acceptor bound exciton can be seen. This excitonic band remains nearly constant in energy between the surface and until 80  $\mu\text{m}$  from the interface and then weakly shifts to blue photon energies. Near the interface, mainly a blue shifted luminescence band at energies larger than the GaN bandgap occurs.

In order to understand the spatial dependency of the luminescence, we performed micro-Raman scattering 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 could determine the strain in our sample as a function of the distance to the substrate (Fig. 3, in the middle). We found that the stress in the GaN layer decreases nearly exponentially with increasing distance from 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 of  $d > 100 \mu\text{m}$ , the layer is fully relaxed. This observation is in good agreement with X-ray diffraction measurements by Hiramatsu et al., on a series of GaN layers also grown on sapphire with varying thickness [8].

Unpolarized low-temperature micro-Raman spectra taken at various distances to the substrate interface taken in  $x(\dots)x$  scattering geometry show that, near the surface of the layer, only the expected GaN Raman modes peaking at about  $533 \text{ cm}^{-1}$  ( $A_1(\text{TO})$ ),  $560 \text{ cm}^{-1}$  ( $E_1(\text{TO})$ ),  $567 \text{ cm}^{-1}$  ( $E_2$ ) and  $742 \text{ cm}^{-1}$  ( $E_1(\text{LO})$ , Fröhlich allowed) are present in the spectra(um) [9]. At a distance of 170  $\mu\text{m}$  (50  $\mu\text{m}$  below the surface) a broader structure below the  $A_1(\text{TO})$ , the  $\text{LPP}^-$  mode, becomes visible. This mode shifts continuously to a

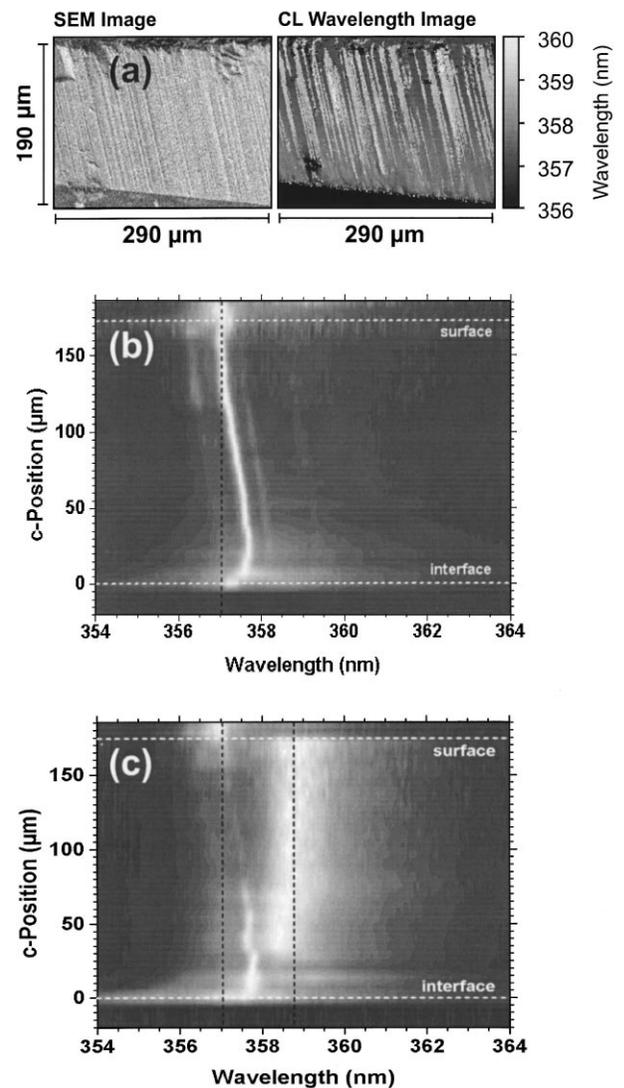


Fig. 2. (a) EEM and CL wavelength image of a thick GaN sample. (b) CL linescan along the dark gray channel. Here, the shift of the free- and donor-bound exciton from the surface to the interface is shown. (c) CL linescan along the light gray channel. The shift behavior of the broad band around the acceptor bound exciton is represented.

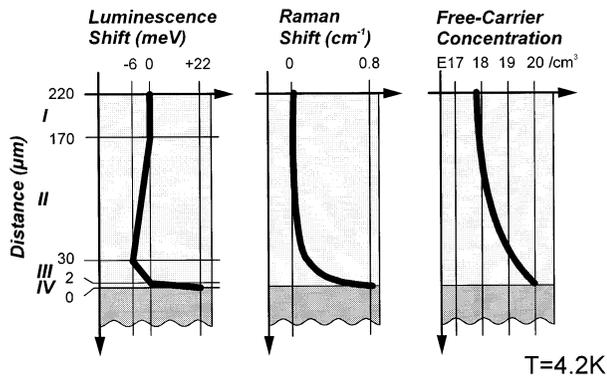


Fig. 3. Shift behavior of the luminescence (left), of the  $E_2$  Raman mode (center) and the free carrier concentration (right) as a function of distance  $d$  to the substrate interface.

higher frequency with decreasing distance to the substrate. Simultaneously, a structure at about  $650\text{ cm}^{-1}$ , known from highly doped GaN [10,11], appears and becomes stronger with decreasing distance, while the  $E_1(\text{LO})$  decreases in intensity. This observation indicates that the free-carrier concentration in the thick GaN layer increases gradually with decreasing distance to the substrate (see Fig. 3, right spectrum). From the energy position of the  $\text{LPP}^-$  mode we were able to estimate the free-carrier concentration according to the procedure described in [10]. The corresponding carrier concentrations for the different distances to the substrate are listed in Fig. 3, left curve. We found that the free-carrier concentration increases from about  $8 \times 10^{17}\text{ cm}^{-3}$ , 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.

#### 4. Discussion

According to the different luminescence shifts, one can divide the layer into four regions (see Fig. 3, left curve). In the first region, for distances in the range of  $220\text{--}170\text{ }\mu\text{m}$ , no shift could be observed; all spectra are quite similar. In the following second region, for distances  $170 > d > 30\text{ }\mu\text{m}$ , the  $I_2$  as well as the free-exciton emission, shifts about 6 meV. This red shift is compensated by the following blue shift in the third region ( $30 > d > 2\text{ }\mu\text{m}$ ). In the fourth region, a peak on the high-energy side of the free-exciton emission line becomes dominating.

While the optical and structural properties of the first region of the GaN layer do not change remarkably 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 the bound- as well as for the 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  $4.2\text{ cm}^{-1}$  [12]. From this one expects a softening of the  $E_2$  mode of about  $0.9\text{ cm}^{-1}$ , which we did not observe in our micro-Raman measurements. In contrast, we found a biaxial compressive strain which reduces exponentially with increasing distance. In the region where the red shift takes place most of the strain is already relaxed (only near the surface the GaN sample is compressively strained). A possible explanation for the red shift of the excitonic luminescence could be a bandgap renormalization induced by the (strong) gradient of the free-carrier concentration which we found by our micro-Raman measurements. Before we focus on this point, we will first discuss the effects in the other regions.

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  $0.8\text{ cm}^{-1}$ , which corresponds to a change of the excitonic energy position of 5.2 meV following the relationship given in [12]. 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 (see Fig. 3). 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 around  $1 \times 10^{20}\text{ cm}^{-3}$ . So 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-to-band transitions, if the Fermi-level is crossing the conduction band (band filling) [13]. Our assignment also agrees with the observations of Cunningham et al. [14], who performed PL measurements on a series of samples with varying doping levels. Eckey et al. [15] also observed this blue shift in their PL measurements where the carrier concentration was induced by high excitation.

We now come back to the discussion of the red shift observed in the second region of the layer. A likely explanation can be given in terms of the inhomogeneous free-carrier distribution in the layer. The gradual increase of the carrier density with decreasing distance to the substrate leads first to a bandgap renormaliza-

tion, which results in a red shift of both excitonic luminescence processes. The built-in stress, which starts for distances  $< 30 \mu\text{m}$  away from the substrate, counteracts this shift. Directly at the substrate interface, in the last  $2 \mu\text{m}$ , the free-carrier concentration reaches a level at which band-to-band transitions takes place.

The observed doping gradient has two reasons. 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 from the substrate. While the high free-carrier density, directly at the substrate, mainly results from the first effect, several groups reported on the formation of amorphous mediate layers at the substrate interface, we believe that the high doping level found  $55 \mu\text{m}$  away from the substrate interface (see Fig. 3) could be explained by indiffusion of Zn or O impurities because of the ZnO buffer layer which disappears after growing GaN on the substrate/buffer layer.

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