

# Raman and Photoluminescence Imaging of the GaN/Substrate Interface

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**Abstract.** GaN exhibits apart from the near-bandgap excitonic and donor-acceptor-pair luminescence a broad "yellow" photoluminescence between 2.0 and 2.5 eV. We performed spatially-resolved photoluminescence and Raman experiments on the substrate interface region of wurtzite GaN layers. We found that the broad photoluminescence band is strong only near the interface. Our investigations reveal that both the substrate interface and a region of structural reorientation of the layer near the interface act as source of the photoluminescence. The Raman-scattering experiments show that at least a portion of the GaN layer near the substrate interface is oriented in such a way that the c-axis of the layer is parallel to the substrate interface. At a distance about 30  $\mu\text{m}$  away from the interface the layer reorients by turning the c-axis by 90° into a direction perpendicular to the substrate interface.

## 1. Introduction

The wide-bandgap semiconductor GaN has attracted considerable attention over the last years because of its application as a basic material for optoelectronic devices working in the blue and UV spectral region, such as blue laser diodes [1]. Apart from the near-bandgap excitonic and donor-acceptor-pair luminescence GaN shows an unwanted broad "yellow" photoluminescence band between 2.0 and 2.5 eV at low temperatures [2]. Recently, intensive work has been done to clarify its origin, and some authors connect this luminescence band with the inherent property of GaN to be automatically n-type conductive [3-5]. However, this issue is still controversial.

Similar luminescence bands are also known from several II-VI semiconductors like ZnS [6]. They are often interpreted as a recombination between shallow donors and deep

acceptors in which the donors or the acceptors were built by anion or cation vacancies. The creation of such intrinsic vacancies is very probable near surfaces, interfaces or grain boundaries.

In order to clarify whether the broad “yellow” photoluminescence band is an intrinsic property of GaN or caused by defects located near the interface to the substrate, we performed spatially-resolved photoluminescence and Raman measurements on hexagonal GaN samples which were grown on sapphire. We found that the luminescence band is strong only in a region near the interface and hence not an intrinsic property of GaN. Our investigations reveal that the photoluminescence originates from both the substrate interface and a region of structural reorientation near the interface where the c-axis of the GaN layer rotates by 90° from a direction parallel into a direction perpendicular to the substrate interface.

## 2. Experiment

The samples investigated were undoped wurtzite GaN layers grown on [0001] sapphire using hydride vapor phase epitaxy (HVPE) with thicknesses of 220 μm, 230 μm and 400 μm and a free carrier concentration of about  $1 \cdot 10^{17} \text{ cm}^{-3}$ . The spatially-resolved photoluminescence and Raman experiments were carried out using a Dilor XY800 triple-grating spectrometer with a charge-coupled device (CCD) detector and confocal optics. The sample was excited either parallel (in-plane) or perpendicular (on-plane) to the substrate surface using the 488 nm (2.54 eV) line of an Ar<sup>+</sup>-Kr<sup>+</sup> mixed-gas laser and the 632.8 nm (1.96 eV) line of an He-Ne Laser. By passing the laser through a microscope objective (x80) the laser beam was focused on a point spot with a diameter of about 1 μm and a power of 2 mW. The scattered light was detected in backscattering geometry which corresponds to an  $x(\cdot)\bar{x}$  configuration for in-plane excitation and a  $z(\cdot)\bar{z}$  configuration for on-plane excitation (under the assumption, that the z is parallel to the c-axis). The samples were cooled down to 4.2 K using an Oxford microscope cryostat. With this setup we obtained a spatial resolution of about 1 μm and a spectral resolution better than 1 cm<sup>-1</sup>.

## 3. Results

The photoluminescence spectra of a 400 μm thick GaN layer taken at 4.2 K and room temperature after excitation at 3.75 eV are compared in Fig. 1. While the spectrum at low temperature is dominated by the excitonic transitions and the donor-acceptor-pair luminescence, the broad photoluminescence band with an intensity maximum at 2.4 eV becomes the dominating part of the room-temperature spectrum.

Figure 2 shows a 40 μm long linescan across the GaN-substrate interface of a 400 μm thick layer where we have taken a spectrum every 1 μm. The region of the substrate is marked by the presence of the A<sub>g</sub> sapphire mode at 419 cm<sup>-1</sup> [7]. The transition to the GaN layer is indicated by the appearance of the A<sub>1</sub>(TO) and the E<sub>2</sub> modes at 534 cm<sup>-1</sup> and 569 cm<sup>-1</sup>, respectively. A photoluminescence band with an intensity maximum at 2.4 eV appears directly at the interface with the substrate; it is seen as constant in Raman shift background, since it is broad compared to the spectral range observed here. The spatial

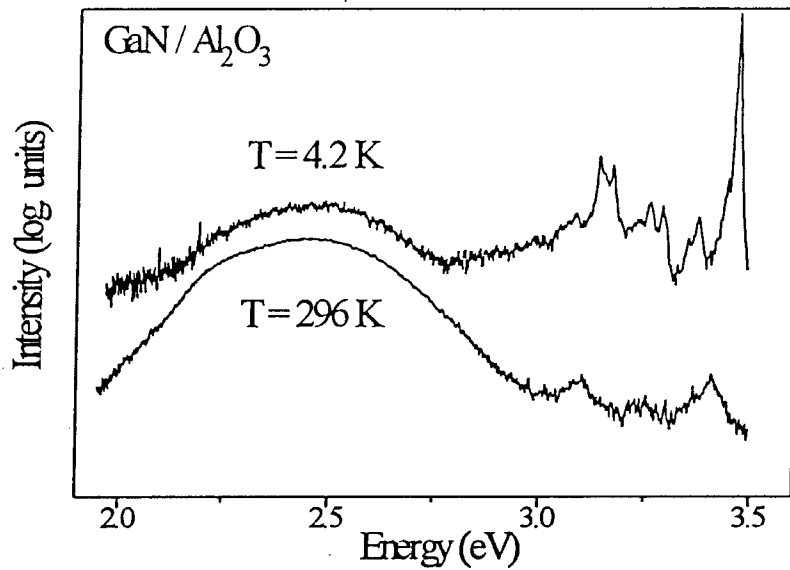


Fig. 1: Photoluminescence spectra of a 400  $\mu\text{m}$  thick GaN layer grown on sapphire taken at 4.2 K and at room-temperature after excitation at 3.75 eV.

width of the region from which this photoluminescence occurs is about 3  $\mu\text{m}$ . The GaN region is dominated by the abruptly increasing  $A_1(\text{TO})$  mode. At a distance  $d$  of about 30  $\mu\text{m}$  away from the substrate interface, in a region several  $\mu\text{m}$  wide, a second broad photoluminescence band appears peaking at the same spectral position as the first photoluminescence band. Simultaneously with the increasing photoluminescence the intensity of the  $A_1(\text{TO})$  Raman signal decreases but the modes continues to be visible.

The spatial continuation of Fig. 2 is shown in Fig. 3 on an expanded spectral and spatial scale. The decrease of the  $A_1(\text{TO})$  Raman signal (near  $d=20 \mu\text{m}$ ) and the broad

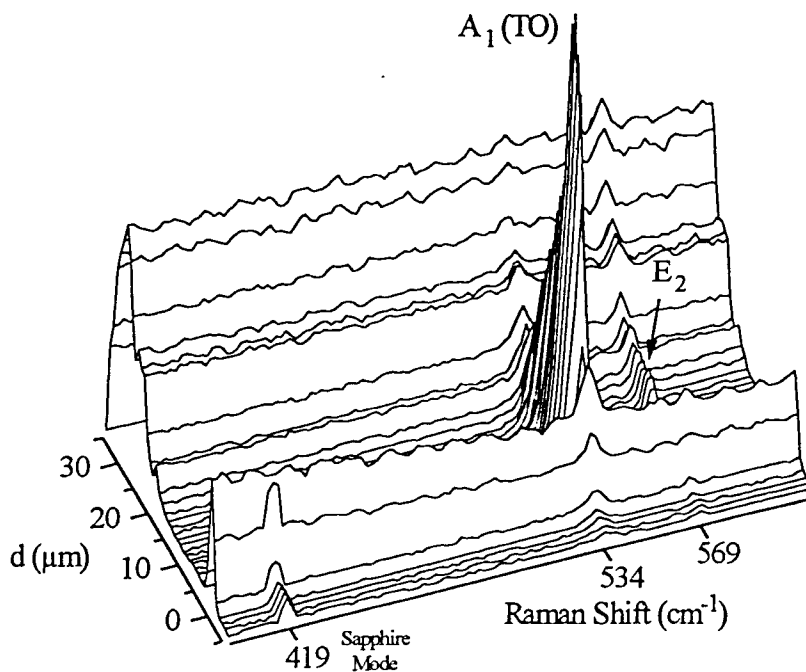


Fig. 2: Linescan across the GaN-substrate interface of a 400  $\mu\text{m}$  thick layer taken at 4.2 K. In order to emphasize the sapphire Raman mode it was multiplied by a factor of 2.

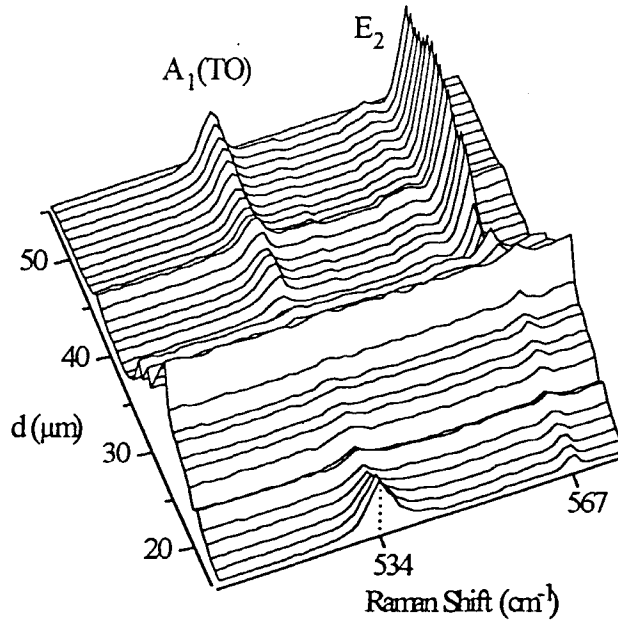


Fig. 3: Spatial continuation of Fig. 2. Linescan across the inner interface caused by a reorientation of the GaN layer taken at 4.2 K. For clarification the spectral scale was enlarged.

photoluminescence band (at  $d = 30 \mu\text{m}$ ) can be seen. Of particular importance is the change in scattering intensity of the different phonon modes. While both, the  $E_2$  mode and the  $A_1(\text{TO})$  mode appear in this region the ratio of their intensity inverts with increasing distance from the substrate interface. We have clarified this in Fig. 4 where we show individual spectra taken at 15, 25 and 50  $\mu\text{m}$ . The strong luminescence was subtracted in the middle spectrum of Fig. 4. The change in intensity starts where the second photoluminescence band appears. While near the interface with the substrate ( $0 \leq d \leq 20 \mu\text{m}$ ) the spectra are dominated by the  $A_1(\text{TO})$  mode the intensity of the  $E_2$  mode increases with the appearance of the second photoluminescence band and becomes the most intensive phonon mode ( $d > 35 \mu\text{m}$ ). The inversion of the relative intensities can be explained by a structural reorientation of the GaN layer. It is interesting to note that the frequencies of both, the  $A_1(\text{TO})$  mode and the  $E_2$  mode decrease by about  $2 \text{ cm}^{-1}$  for distances larger than  $25 \mu\text{m}$  (Fig. 3), which is likely to be caused by strain relaxation. This is consistent with the results of Kozawa et al. [8] who observed a decrease of  $\sim 1 \text{ cm}^{-1}$  for increasingly relaxed GaN layers.

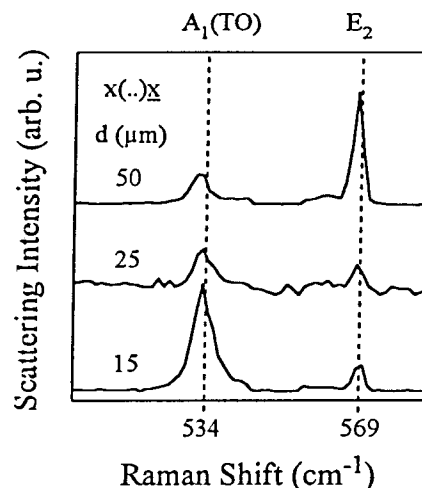


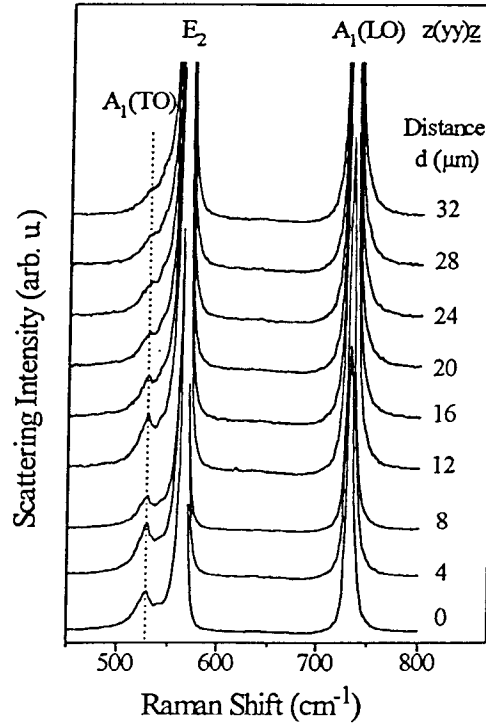
Fig. 4: Raman spectra of the 400  $\mu\text{m}$  thick GaN layer taken at various distances  $d$  from the interface with in-plane excitation. The red shift can be explained by strain relaxation.

**Table 1:** Raman selection rules for backscattering configuration used in this work. The c-axis is parallel to the z direction.

Scattering Configuration	Allowed Modes
$z(yy)\bar{z}$	$A_1(\text{LO}), E_2$
$x(zz)\bar{x}$	$A_1(\text{TO})$
$x(yz)\bar{x}$	$E_1(\text{TO})$

In Table 1 the selection rules for first-order Raman scattering of hexagonal material and in-plane excitation are listed [9, 10]. Comparing Table 1 with the corresponding Raman spectra in Fig. 4 reveals that for the region near the substrate interface ( $0 \leq d \leq 20 \mu\text{m}$ ) where the spectra are dominated by the  $A_1(\text{TO})$  mode the GaN layer is oriented in such a way that the scattering geometry corresponds to  $x(zz)\bar{x}$ . For  $d > 35 \mu\text{m}$  the  $E_2$  mode is the strongest mode and the  $A_1(\text{TO})$  is still observable. This combination corresponds to  $x(yy)\bar{x}$ . Since the incident polarization of the exciting laser remained parallel to the substrate interface and constant throughout the experiment our results show that the c-axis of the GaN layer near the substrate is parallel to the interface and turns by about  $90^\circ$  at a larger distance ( $d > 20 \mu\text{m}$ ) from the interface. This becomes more clear when considering

Fig. 5 in which a depth profile of room-temperature Raman spectra taken in  $z(yy)\bar{z}$  configuration on a  $220 \mu\text{m}$  thick layer are plotted. By using the 632.8 nm line of a He-Ne laser no photoluminescence was excited. The confocal optics allows to record Raman spectra at several depths, i. e. distances to the substrate interface. All spectra are dominated



**Fig. 5:** Depth profile of a  $220 \mu\text{m}$  thick GaN layer. The Raman spectra are taken at room temperature using the 632.8 nm line of a He-Ne laser.

by the  $E_2$  and the  $A_1(\text{LO})$  modes but near the substrate interface the  $A_1(\text{TO})$  mode can clearly be seen. The scattering intensity decreases with increasing distance to the interface. According to the selection rules listed in Tab. 1 the  $A_1(\text{TO})$  is only excitable if the c-axis lies perpendicular to the incident wave vector. Hence it follows from both in- and on-plane Raman measurements that at least a portion of the GaN layer near the interface to the substrate is oriented parallel to it. This reorientation yields a further interface which like the substrate interface acts as source of the broad luminescence band.

#### 4. Conclusions

We have shown that the origin of the broad photoluminescence band with an intensity maximum at 2.4 eV is not homogeneously distributed in our GaN layers. Instead, we found that the luminescence is strong only near the interface region. A first luminescence band appears directly at the interface with the substrate, a second one appears approximately 30  $\mu\text{m}$  away from the interface in a region which is several  $\mu\text{m}$  wide. Simultaneously performed Raman scattering experiments allowed us to analyze layer orientation and strain and revealed that the second band appears where a significant reorientation of the wurtzite GaN c-axis from parallel to perpendicular to the substrate surface occurs. This observation suggests that the 2.0 - 2.5 eV luminescence is not intrinsic to GaN but occurs primarily near structural defects.

#### 5. Acknowledgments

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