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# Green coloring of GaN single crystals introduced by Cr impurity

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## Abstract

In this study unintentionally doped GaN grown by hydride vapor phase epitaxy that exhibits a sharply delimited region of green color was investigated. Optical analysis was performed by absorption and photoluminescence spectroscopy. An absorption band between 1.5 and 2.0 eV was found to be responsible for the green color and was related to a sharp emission at 1.193 eV by luminescence and excitation spectroscopy. The appearance of both optical signatures in the region of green color was related to an increase of Cr contamination detected by secondary ion mass spectrometry. We propose that the origin of green color as well as the emission line at 1.193 eV is attributed to internal transitions of Cr<sup>4+</sup>.

*Keywords:* Crystal impurities, Bulk GaN, Hydride vapor phase epitaxy, Absorption spectroscopy, Photoluminescence spectroscopy

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## 1. Introduction

Transition metal (TM) doping of Gallium Nitride (GaN) has attracted great interest over the last decade for the purpose of fabricating semi-insulating GaN based buffer layers for device structures [1, 2] as well as in the field of diluted magnetic semiconductors [3, 4, 5, 6, 7] or intentional Cr-doping [8, 9, 10, 11]. The influence of TM contamination on the crystal quality and optical properties of unintentionally doped (UID) GaN are rarely discussed [12, 13, 14, 15, 16] although TM may deteriorate both. TMs may introduce optical transitions reducing the transparency of the material as recently reported for Mn contamination [17]. However, the substrate transparency is a prerequisite for optimal light output and thus optimized performance of optoelectronic devices [18, 19]. Furthermore, TMs act as minority carrier lifetime killer [20]. It is therefore of great interest to identify impurities resulting in reduced transparency in the visible spectral region. Several mechanisms involving TMs are considered to contribute to absorption bands in the visible spectral range: transitions between the TM defect level and the host's bands and internal transitions between TM d-levels whose degeneracy is (partially) lifted by interaction with the crystal field of the surrounding matrix [21, 22]. Sometimes those absorption processes result in coloring of the crystal, thereby strongly reducing its transparency. The described absorption bands are often accompanied by sharp emission lines observed in photoluminescence (PL) being internal radiative transitions between the first excited state and the ground state of the TM ion [21]. As the transition energies are characteristic for the interaction of the specific TM ion with the matrix, complementary optical methods may be applied to identify centers responsible for reduced transparency.

In this paper, we study the correlation of the green coloring with transition metal contamination during GaN growth. Optical spectroscopy in conjunction with element analysis is used to identify the corresponding impurity.  $\text{Cr}^{4+}$  was previously suggested to be responsible for the 1.193 eV luminescence emission [15, 23] and is now shown to be the reason of the green coloring.

## 2. Experimental

The bulk freestanding GaN crystal shown in Fig. 1a was grown in a commercially available vertical HVPE reactor [24], similar to the one presented

in reference [25]. The UID crystal shows strongly reduced transparency in its central part. An  $\langle 1\bar{1}00 \rangle$  (m-plane) cross section prepared from the central part of the crystal is presented in Fig. 1b and indicates that the effect of reduced transparency is limited to a sharply delimited region close to the substrate-GaN interface. The m-plane cross section of the crystal was mechanically polished to optical grade prior to PL, PL excitation (PLE) and absorption spectroscopy. High resolution X-ray diffraction measurements were carried out with  $\text{CuK}\alpha 1$  radiation on a triple-crystal Seifert/FPM diffractometer equipped with an Eulerian cradle, a sealed X-ray tube with a copper anode, and two dislocation-free (111)-oriented Si crystals acting as monochromator of the primary beam and analyzer of the diffracted beam. By performing the diffraction measurement with  $(0.09 \times 2)$  mm<sup>2</sup> large primary beam, the instrumental broadening of the diffractometer was estimated as 12 arc-sec. Absorption spectroscopy measurements at room temperature and 80 K were performed in the wavelength range of 350 to 1000 nm using a Specord 600 UV-VIS spectrometer. PL excited by a 325 nm HeCd laser was performed at 15 K and room temperature in the range of 340 to 1100 nm with excitation power densities of  $8.5 \text{ W cm}^{-2}$  and  $23 \text{ W cm}^{-2}$ , respectively. PLE was excited by a NKT SuperK Extreme supercontinuum laser with a tunable bandpass filter in the range of 500 to 850 nm and measured at various temperatures. PLE spectra were normalized with respect to the laser excitation power density. PL and PLE spectra were detected by a 0.5 m monochromator equipped with a liquid nitrogen cooled CCD camera and corrected for spectral response of the system. Room temperature PL line scans along the optical axis of an m-plane cross section were either performed with the standard PL setup for detection of the near infrared part of the spectra or with a  $\mu$ -PL setup with the laser spot focused to a diameter of 1  $\mu\text{m}$  for the ultraviolet part of the spectra. The latter was detected by a 0.8 m monochromator equipped with a thermoelectrically cooled CCD camera. The spectral resolution of the PL setup is about 0.5 meV in the NIR spectral range. Secondary ion mass spectrometry (SIMS) was performed to detect transition metal contamination. Only a qualitative measure of impurities can be extracted from those measurements due to the lack of a TM implanted reference sample.

### 3. Results

The observed green color is limited to a sharply confined layer of 270  $\mu\text{m}$  width close to the substrate-GaN interface, as can be seen in Fig. 1b. During

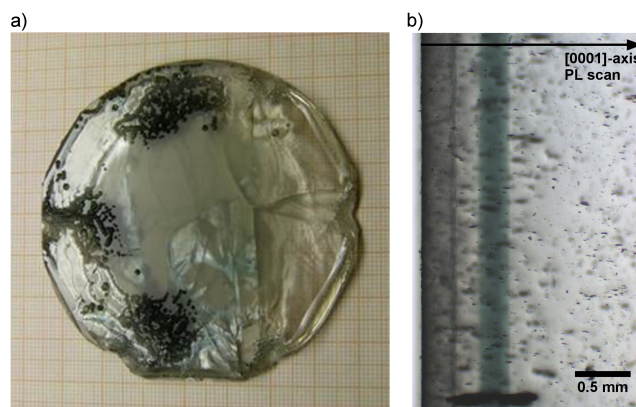


Figure 1: a) Freestanding bulk GaN crystal exhibiting reduced transparency in the central part. b) Transmission micrograph of an m-plane cross section of the central part of the crystal shown in a). The transparency is strongly reduced in a layer of 270  $\mu\text{m}$  width close to the substrate-GaN interface by green coloring. The arrow indicates the direction of PL linescans parallel to the crystal [0001]-axis (c-axis).

the beginning of HVPE growth several growth steps under varying growth conditions are employed to optimize the nucleation and to reduce the threading dislocations density resulting in the layered structure observed. Cr may have been introduced into the GaN lattice during unintentional damage of a thermocouple close to the substrate holder. The coating of the thermocouple consists of Cr and Ni components, which were thus probably incorporated into the growing GaN layer. However, the additional source of unintentional doping apparently only amplifies the effects described in the following sections. Once recognized, similar but weaker coloring was observed in several GaN crystals grown prior and after the one discussed here.

High resolution X-ray diffraction measurements were performed to investigate the structural quality of the grown crystal. The positions of  $00l$  ( $l = 2, 4$  and  $6$ ) and  $110$  reflexes recorded in  $\omega - 2\Theta$  direction enabled us to determine the lattice parameters of GaN as  $a = 3.1905 \text{ \AA}$ ;  $c = 5.1858 \text{ \AA}$ .  $006$  and  $110$  reflexes revealed a certain asymmetry that can be related to an inhomogeneous distribution of the impurity atoms inside the GaN matrix. Compared to the relaxed GaN lattice parameters [26], the  $a$  lattice parameter is slightly enlarged due to the incorporation of transition metals [12, 27]. However, the crystal exhibits a good quality with a total threading dislocation density of about  $10^6 \text{ cm}^{-2}$  as was obtained from the full width at half maximum values

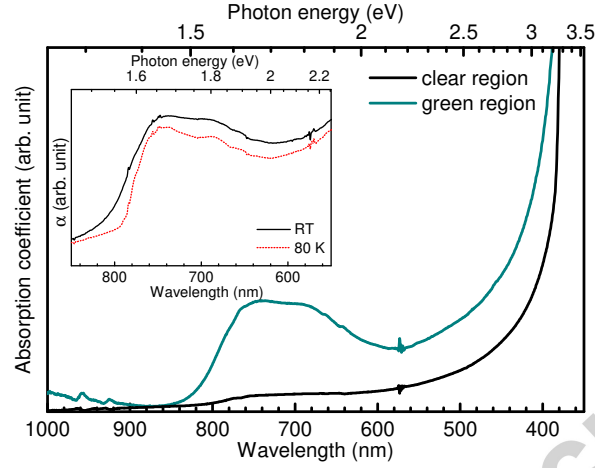


Figure 2: Absorption coefficient traces recorded at room temperature at spots located mostly inside (upper curve, green) and outside (lower curve, black) of the green region, inset: absorption measurements at 80 K compared to room temperature.

of  $00l$  and  $110$  rocking curves.

Room temperature absorption spectroscopy was performed at spots localized mostly inside and outside of the colored layer. Low temperature measurements were conducted on a  $c$ -plane piece of the sample. The corresponding spectra are shown in Fig. 2 and its inset. Compared to the transparent region, the spectrum of the green stripe shows an additional broad absorption band between 1.5 and 2.0 eV (800 - 600 nm) which may consist of up to three bands, limiting the transmission to the green to violet region. Measurements at liquid nitrogen temperature compared to room temperature (inset of Fig. 2) further strengthen the existence of three absorption bands. Moreover, the absorption in the high energy part of the spectrum (blue to ultraviolet) is also increased due to photoionization of deep native or impurity related defects. The interplay of the absorption peak between 1.5 and 2.0 eV and the overall increase in absorption above 2.0 eV results in a minimum of absorption in the green spectral region and consequently explains the observed green color with grey shade.

To identify the origin of the absorption peak between 1.5 and 2.0 eV PL measurements were performed. Typical PL spectra recorded in the clear part of the  $m$ -plane cross section are depicted in Fig. 3a). At 15 K the near band edge emission (NBE) (labeled with A) consisting of excitonic peaks at

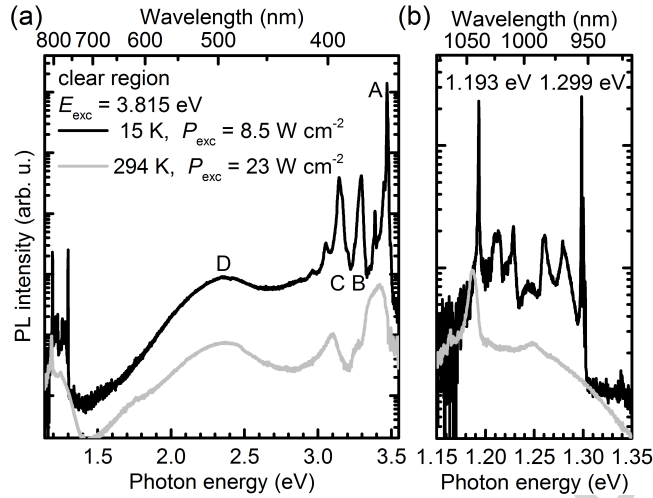


Figure 3: PL spectra recorded at 15 K and room temperature on the clear part of an m-plane cross section of the crystal. a) Spectra recorded over a wide spectral range including NBE (A), transitions related to structural defects (B, C) and point defect related emission (D). b) Enlargement of the near infrared spectral region with transitions related to ZPL.

3.474 eV and 3.482 eV that are related to donor bound excitons and the free A exciton, respectively, is the most intense contribution to the PL spectrum. All other contributions are weaker by at least one order of magnitude indicating high quality of GaN in the clear part of the sample. The lower energetic peaks B and C at 3.294 eV and 3.142 eV are typically observed in regions of high density of basal plane stacking faults and are attributed to excitons bound to those extended defects [28, 29, 30]. The latter is accompanied by two LO phonon replica at 3.054 eV and 2.963 eV. Furthermore, a broad defect band D can be observed around 2.39 eV. This band is usually detected in high quality HVPE GaN at high excitation power densities and is related to electron transitions via C atoms substituting for an N site ( $C_N$ ) [31]. As specific internal transitions in TM centers are expected in the near infrared spectral region the respective part of the spectra is enlarged in Fig. 3b). The transitions with zero phonon lines (ZPLs) at 1.299 eV and 1.193 eV visible at 15 K are attributed to internal transitions in  $Fe^{3+}$  and  $Ti^{2+}$  or  $Cr^{4+}$ , respectively. The peak at 1.299 eV is caused by an internal transition in  $Fe^{3+}$  [32] and accompanied by a pronounced phonon side band at lower energies. The second sharp transition is observed at 1.193 eV. This line is attributed to an internal transition of a  $d^2$ -electron center, possibly  $Ti^{2+}$  [33]



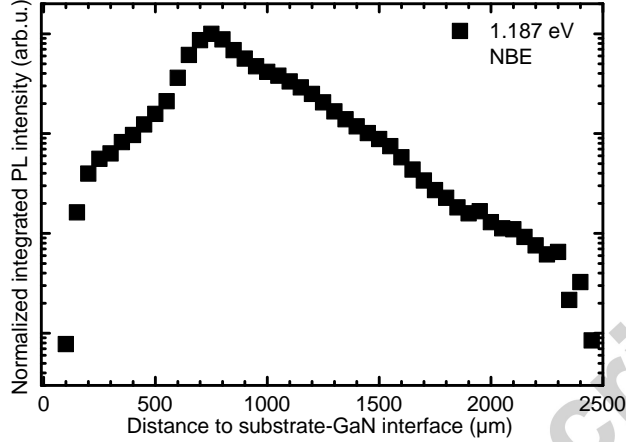


Figure 4: Integrated intensities of the NBE and 1.187 eV transition derived from PL spectra recorded at room temperature on the m-plane cross section of the sample at different distances from the substrate-GaN interface. At a distance of 750  $\mu\text{m}$  the NBE is strongly suppressed whereas the intensity of the 1.187 eV line is maximal. This region corresponds to the location of the green color.

or  $\text{Cr}^{4+}$  [15]. In order to investigate spectral changes in different regions of the crystal, a linescan parallel to the growth direction was performed on the m-plane cross section shown in Fig. 1 (b) at room temperature. As shown in Fig. 3 all major PL contributions except the transitions related to structural defects can also be observed at room temperature. The NBE is broadened and red shifted to 3.41 eV due to the temperature induced narrowing of the bandgap [13]. In the near infrared the iron related ZPL is merged with the phonon side band forming a peak around 1.25 eV whereas the ZPL at 1.193 eV is only slightly broadened and red shifted to 1.187 eV as it was also observed by Heitz et al. [33].

Normalized integrated PL intensities of the NBE and the sharp transition at 1.187 eV as function of the distance to the substrate-GaN interface of the m-plane cross section are depicted in Fig. 4. The NBE intensity is strongly reduced during the first stages of growth reaching a minimum value at approximately 750  $\mu\text{m}$ . The intensity drop may be explained by an increase of non-radiative centers related to extended defects or deep charge carrier traps that are typically introduced by TM contamination [5]. This is supported by the simultaneous intensity increase of the TM related 1.187 eV

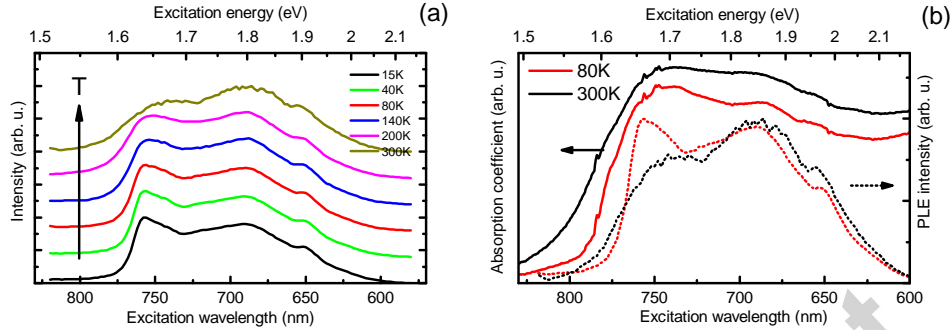


Figure 5: (a) PLE spectrum of the 1.193 eV ZPL recorded at various temperatures. An excitation peak exhibiting triplet structure is observed between 1.5 and 2.0 eV. (b) PLE spectra in comparison with the absorption spectra.

emission. Scanning further parallel to the  $c$ -axis, approaching the (0001) surface (Ga-face) the 1.187 eV intensity continuously decreases whereas the NBE partially recovers to a constant value. The very high initial NBE intensity may be explained by an increased oxygen incorporation during the first stages of growth [34]. The region of lowest NBE and highest 1.187 eV emission coincides with the position of the delimited range of green color indicating that either  $\text{Ti}^{2+}$  or  $\text{Cr}^{4+}$  are responsible for the observed green color.

The excitation spectrum of the respective PL line for various temperatures is depicted in Fig. 5 (a) and reveals a complex structure of at least three overlapping peaks. At all temperatures a triplet peak structure can be resolved that is shown to be comparable to the absorption spectra, see Fig. 5 (b). Thus, the increased absorption between 1.5 and 2.0 eV and the PL transition at 1.193 eV can be attributed to the same TM center that is also responsible for the observed green color.

In order to verify the origin of the optical signatures observed, SIMS was performed on the  $m$ -plane sample cross section. The analysis was limited to TMs that may be present in  $d^2$ -electron configuration in GaN, namely  $\text{Ti}^{2+}$ ,  $\text{V}^{3+}$  and  $\text{Cr}^{4+}$ . Due to the lack of a TM implanted GaN reference sample merely qualitative analysis was possible comparing data recorded at different spots across the sample cross section, specifically at spots in the clear sample region, at the boundary between clear and green region and in the green region. For the sake of clarity only data recorded in the clear and the green spot are depicted in Fig. 6. The concentrations of V and Ti remain close

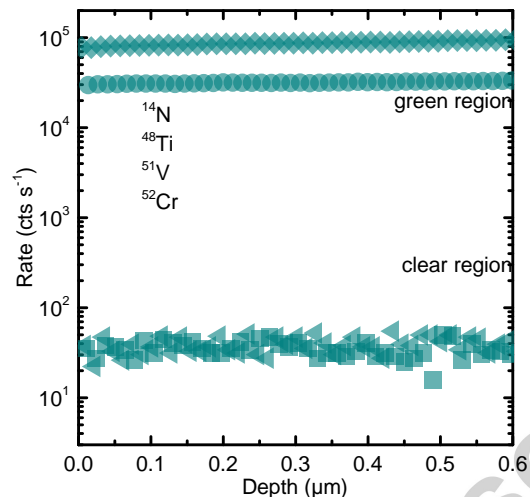


Figure 6: SIMS profiles of nitrogen and transition metals with possible  $d^2$ -electron configuration recorded at two spots across the m-plane cross section: in the clear sample region (open symbols) and in the green region (compact green symbols).

to the detection limit for all spots investigated with a slight increase of Ti directly in the green region. However, a gradual increase of over an order of magnitude is found for Cr towards the green region with the maximal concentration found on the green spot. The Cr concentration thus follows the same trend as the intensity of the PL line at 1.193 eV.

#### 4. Discussion

The optical analysis shows that the green color in the investigated UID-HVPE GaN sample is caused by an absorption band between 1.5 and 2.0 eV. Transmission is thus limited to the green to violet spectral region explaining the color effect. Additionally, increased absorption in the blue to ultraviolet spectral region results in a grey shade of the observed color. As already pointed out in Section 3, several photoionization processes can participate in the formation of the absorption band above 2.0 eV. PL measurements unambiguously show contamination with Fe in addition to the TM center responsible for green color. Thus, it is likely to assume a contamination by various TM impurities. Those impurities may not necessarily exhibit characteristic radiative internal transitions but can cause broad structureless absorption bands due to photoionization starting or ending at the defect level

within the GaN bandgap. As indicated by the TM related PL intensities, the TM contamination in the green part of the sample is higher compared to the contamination in the transparent regions. Due to the position of their defect level in the GaN bandgap Fe and Mn are known to cause absorption bands with energy onsets at 2.8 eV [32] and 1.8 eV [22], respectively. Those bands may participate in an increased absorption in the blue to ultraviolet spectral region.

The structure of the absorption band between 1.5 and 2.0 eV strongly resembles the excitation spectrum of the emission line detected at 1.193 eV in PL measurements. This line was first reported by Heitz et al. [33, 35] and Baur et al. [15], and attributed to an internal transition of a  $d^2$ -electron center by analysis of the level fine structure observed in a magnetic field. Heitz et al. attributed this emission line to an internal transition in  $Ti^{2+}$  by doping experiments. However, Baur et al. assigned the 1.193 eV ZPL to  $Cr^{4+}$ . The observed emission is strongly increased in the green region. Our SIMS analysis reveals a strong increase of Cr signal in the region of green color, that is also associated with an increase of the ZPL at 1.193 eV. Consequently, our analysis supports the assignment to an internal transition in  $Cr^{4+}$  in agreement with reference [15, 23]. A comparison with other III/V semiconductors shows the  $Cr^{4+/3+}$  donor level typically to be at energies between the  $Mn^{3+/2+}$  and  $Fe^{3+/2+}$  acceptor levels whereas the respective  $Cr^{3+/2+}$  acceptor level is usually close to the conduction band [23, 36]. Assuming the respective energies of 2.86 eV [32] and 1.8 eV [22] above the valence band edge for the  $Fe^{3+/2+}$  and  $Mn^{3+/2+}$  level in GaN, the  $Cr^{4+/3+}$  level can be expected to be between 1.8 eV and 2.8 eV above the valence band edge. As optical signatures of the  $Mn^{3+}$  center can be observed in UID GaN [17], it is not unlikely to observe  $Cr^{4+}$  related signatures. Detailed analysis of the splitting of the ZPL at 1.193 eV in magnetic fields by Koehl et al. [37] finds typical characteristics of a singlet to triplet transition. The ZPL can thus be attributed to the  ${}^1E(D) \rightarrow {}^3A_2(F)$  internal transition in  $Cr^{4+}$ . This also explains the minor line broadening and red shift of the ZPL in the temperature range between 15 K and room temperature, as the energy of the first excited state  ${}^1E(D)$  is basically constant over a wide range of crystal field energies. It is therefore hardly affected by strain variations, as derived by the canonical coordination chemistry energy diagram of a  $d^2$  electronic center in tetrahedral symmetry developed by Tanabe and Sugano [38].

As already mentioned in Section 1 the absorption peaks observed between 1.5 and 2.0 eV can be attributed to photoionization bands or to internal

transitions into higher excited states. The triplet peak structure detected in the related PLE spectra allows us to exclude photoionization from or to the  $\text{Cr}^{3+/4+}$  level as origin of the observed absorption band. However superimposed photoionization processes may induce broadening of the bands [23] as known from  $\text{Cr}^{4+}$  optical absorption processes in GaAs [39]. As shown for Mn in GaN [40], photoionization processes ( $\text{Mn}^{4+} \rightarrow \text{Mn}^{3+} + h^+$ ) can overlap internal transitions to excited states. The intracenter transitions in  $\text{Mn}^{4+}$  ( ${}^4\text{T}_1(\text{F}) + h\nu \rightarrow {}^4\text{T}_1(\text{P})$ ) have comparable spectral width which are similar to the ones observed in our PLE spectra. The triplet structure of the absorption band and the PLE spectrum is characteristic for transitions from orbital singlet to triplet states induced by a dynamic Jahn-Teller interaction [41]. Similar absorption lineshapes have been observed in a variety of systems. Especially  $\text{V}^{3+}$ , another  $d^2$  center, shows comparable absorption spectra in several III/V compounds [42, 43] and the lineshape is explained by a strong coupling to modes of mainly  $t_2$  symmetry. Furthermore, Koehl et al. proved resonant pumping of the 1.193 eV luminescence, indicating that the center is already present in its radiative charge state and no charge transfer process is necessary to observe this emission line. Thus, we conclude that the absorption peak is caused by an internal transition to higher energy excited states ( ${}^3\text{T}_1(\text{F})$  and sublevels) of the  $\text{Cr}^{4+}$  center. The experimentally determined values of absorption peaks at 1.62 eV and 2.8 eV [15, 33, 35] are in good agreement with theoretically determined energy splittings between the  ${}^3\text{A}_2(\text{F})$  ground state and the higher excited states  ${}^3\text{T}_1(\text{F})$  and  ${}^3\text{T}_1(\text{P})$  [44]. Based on this analysis the absorption peak between 1.5 and 2.0 eV that is responsible for the green color is assigned to the  ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_1(\text{F})$  internal transition in  $\text{Cr}^{4+}$  whereas the respective transition into the  ${}^3\text{T}_1(\text{P})$  level may contribute to the increased absorption above 2.0 eV.

The investigated GaN crystal has probably been contaminated with Cr by a damaged thermocouple. However, reduced transparency with very similar optical signatures were detected in several other samples. TMs are frequently observed impurities in HVPE GaN [17, 37] possibly originating from hot reactor steel parts. In our case those parts are manufactured by a type of stainless steel, which contains a considerable amount of Cr. As the absorption band responsible for green color is specifically related to Cr in charge state  $4+$ , not only the Cr concentration but also the position of the Fermi level within the GaN bandgap is relevant for the observation of green color. The sharp confinement of the sample region exhibiting green color points to a complex interplay of Cr incorporation, growth conditions and Fermi level

position to allow the green color to occur.

## 5. Conclusion

The origin of a spatially distinct green color in UID-HVPE grown GaN was investigated by absorption and luminescence spectroscopic methods as well as by SIMS. Absorption spectroscopy revealed an absorption band between 1.5 and 2.0 eV that is responsible for the observed green color. This absorption band is related to a PL line at 1.193 eV that is also strongly increased in the region of green color. By additional qualitative SIMS, the absorption band and the ZPL at 1.193 eV, could be related to a contamination with Cr. According to the presented analysis, internal transitions in  $\text{Cr}^{4+}$  are responsible for both, the PL line observed at 1.193 eV as well as the absorption that is responsible for the observed green color.

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